CAPILLARY FLOW REACTOR FOR SELECTED DYE-ASSISTED SOLAR PHOTOCHEMICAL REACTIONS

BY

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The success of the work is dedicated to Almighty Allah and my family (The Sarumi's) for their continuous prayer, support, and encouragement throughout my stay in the kingdom.

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In the beginning, Allah is the overseer of all activities. Nothing prevails without His authorization and nothing shall succeed without His sole approval and preordainment. Gratitude goes to Him alone for giving me the strength to cross the hurdles regardless of the heights.

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LIST OF ABBREVIATIONS

RB:	Rose Bengal
O.D	Organic Dye
U.V	Ultraviolet
SET:	Single Electron Transfer
NMR:	Nuclear Magnetic Resonance
HPLC:	High Performance Liquid Chromatography
ACN:	Acetonitrile
PPM:	Parts Per Million
TLC:	Thin Layer Chromatography
TBADT	Tetrabutylammonium decatungstae
KCN	Potassium cyanide
ISC	Intersystem crossing
LEDs	Light emitting diodes
IC	Internal conversion
S	Singlet state
T	Triplet state

hν	Photons energy

ABSTRACT

Full Name : [ISMAILA ABDULKAREEM YUNUS]

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A capillary flow reactor was fabricated and tested on few organic reactions using dye as catalyst (metal-free) under sunlight irradiation. Organic dyes are cheap, non-polluting, environmentally friendly and can be modified easily unlike metal photoredox catalysts. The reaction progress was monitored using high-performance liquid chromatography (HPLC) and thin layer chromatography (TLC). Kingdom of Saudi Arabia is blessed with high intensity of solar energy throughout the year; annual average solar radiation received on the Arabian Peninsula, in general, is about 2200 kWh/m^2. In this study, we carried out three different reactions: Dehydrogenative coupling reaction, Photoacylation reaction and finally cyanation reactions. We achieved a moderate to good yield with 43%, 64% and 80% for dehydrogenative coupling, photoacylation, and cyanation reaction respectively. The results were in good agreement with the literature. For the first time, we showed the effect of reactor size on the reaction yield for the cyanation reaction. We fabricated three different reactors with 3.0, 7.5 and 11.0m capillary length and observed a decrease in reaction time with an increase in the reactor size as a form of scale up, and we studied cyanation reaction using an organic dye and acetic acid (cocatalyst) with an acyclic tertiary amine. This work stands as a support for the claim made by Rueping et al who conducted their study with a derivative of an acyclic amine: that acyclic amine derivatives are also viable in this type of

reactions and not restricted to the tetrahydroisoquinoline derivatives alone which are abundant in literature.

ملخص الرسالة

الاسم الكامل: إسماعيل عبدالكريم يونس

عنوان الرسالة: مفاعل التدفق الشعري للتفاعلات الكيميائية الضوئية الشمسية لأصباغ مختارة

التخصص: الكيمياء

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تم تصنيع واختبار مفاعل تدفق شعري على بعض التفاعلات العضوية باستخدام أصباغ كمحفزات (خالية من الفلزات) تحت إشعاع الشمس. الأصباغ العضوية رخيصة الثمن, وغير مسببة للتلوث, وصديقة للبيئة كما أنه يمكن عمل بعض التعديلات عليها بسهولة على عكس محفزات الأكسدة والإختزال الفلزية. تم متابعة تقدم التفاعل باستخدام الفصل الكروماتوجرافي السائل عالي الأداء, والفصل الكروماتوجرافي بالطبقة الرقيقة. تتميز المملكة العربية السعودية بشدة عالية لأشعة الشمس على مدار العام, حيث يصل متوسط الإشعاع المتلقى على منطقة شبه الجزيرة العربية في العموم إلى 2200 كيلو وات في الساعة/ متر مربع. في هذه الدراسة. تم تنفيذ ثلاثة تفاعلات مختلفة: الإقتران بإزالة الهيدروجين, تفاعل الأسيلة الضوئية, وأخيراً تفاعل إضافة السيانيد. تم التحصل على نتائج متوسطة إلى جيدة بمعدل انتاجية 43%, 64% و 80% للتفاعلات الثلاثة بالترتيب السابق ذكره. هذه النتائج على وفاق مع ما تم من أعمال بحثية أخرى, وللمرة الأولى , بيّنا تأثير حجم المفاعل على إنتاجية تفاعل إضافة السيانيد, حيث قمنا بتصنيع ثلاثة مفاعلات بأطوال شعرية مختلفة 3.0, 7.5 و 11 متر وتم ملاحظة تقليص زمن التفاعل مع زيادة طول المفاعل, كما تم دراسة تفاعل إضافة السيانيد باستخدام ضبغ عضوي مع حمض الخليك (كمساعد محفز) مع ثلاثي أمين غير حلقي. هذا العمل يمثل إثبات ودعامة للعمل المنجز من قبل روبين وفريق العمل الذين قاموا بالدراسة على مشتق من أمين غير حلقي, مشتقات الأمين تلك أيضاً صالحة للإستخدام في هذه التفاعلات وليس مقتصرة على مشتقات (تتراهيدرو أيزوكينولين) فقط المتواجدة بكثرة في الأعمال العلمية المنشورة.

CHAPTER 1

INTRODUCTION

1.1 Background

Photochemical reactions in organic chemical synthesis are commonly cleaner and more effective than other types of reactions since the main reagent is light of certain energy [1].

Following the depletion of non-renewable energy resources, the demand for alternative sources such as the wind, geothermal and solar energy sources will demonstrate admirable significance role in the nearest future. Particularly, this is ascertained for the solar energy, which can be converted into the chemical form of energy with the aid of solar assisted reactions. Photocatalysis is one of the most widely studied of the solar photochemical reactions and finds its applications in various industries as fine chemical production, construction and architecture, air and water treatment etc. [2].

The products of photocatalysis were first marketed in the mid-1900s in japan and spread to America and Europe [3]. As at 2009, the volume of solar photocatalyzed products in the global market was $848 million which was expected to show a double in its value in 2014, amounting to about $1.7 billion [3].

The application of solar energy in the synthesis of organic compounds had not been explored not until in the early 20^{th} century when the father of modern photochemistry

Ciamician began to study the chemical behavior of organic compounds when subjected to solar irradiation. The technical-scale production of ascaridole (an anthelmintic drug) using solar photochemistry by Schenck in 1943 by the irradiation of alpha-terpinene using solar energy was one of the first breakthrough in the use of solar based photochemistry [3].

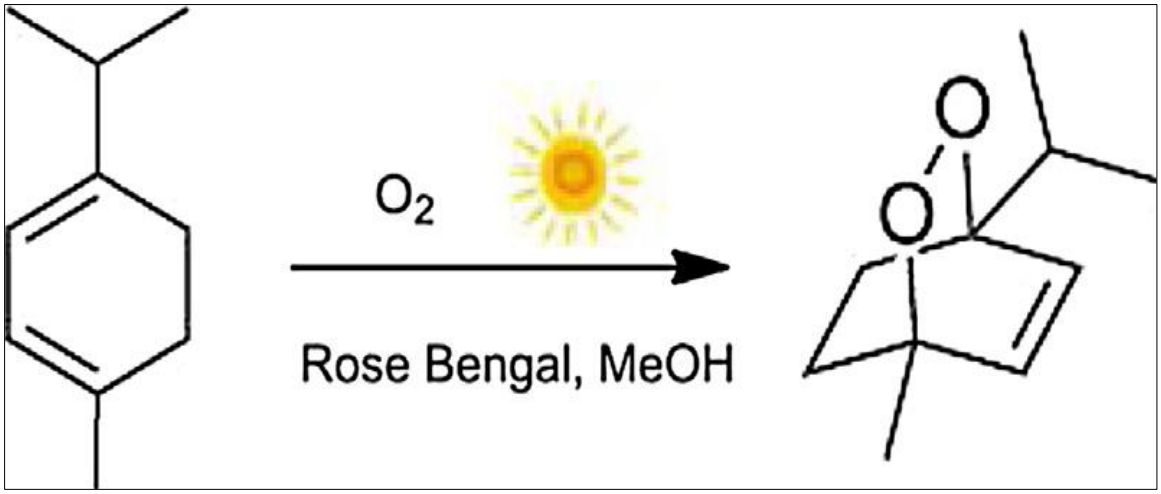

Figure1-1: Production of ascaridole [3].

The pioneer solar chemical plant to produce ascaridole was set up after the completion of the World War II [4]. In the second phase of the 20th century, accompanied by the growth of artificial lamps took photochemistry back to the laboratory (indoors). In the 1970s, following the oil crisis, and the effect of global warming, the use of sunlight as a source of energy was greatly strengthened and motivated continuous research. In the course of these years, the market perspective of heterogeneous photocatalyst was shown in the global market [3, 4]. The rebirth in the interest of solar energy production led to the design of new concentrating and non-concentrating solar photoreactors.

Numerous experiments were carried out in the detoxification of aqueous effluents using solar energy during the early 1990s [3]. The pioneer experimental solar plant was first designed and built in Albuquerque (New Mexico, USA) in the year 1989 [5]. A similar resource was built proximately in 1990 at the Plataforma Solar de Almeria (Almeria in Spain). Applied research has shown a basis in the use of natural sunlight since the era of the 21st century for the production of preindustrial fine chemicals [6].

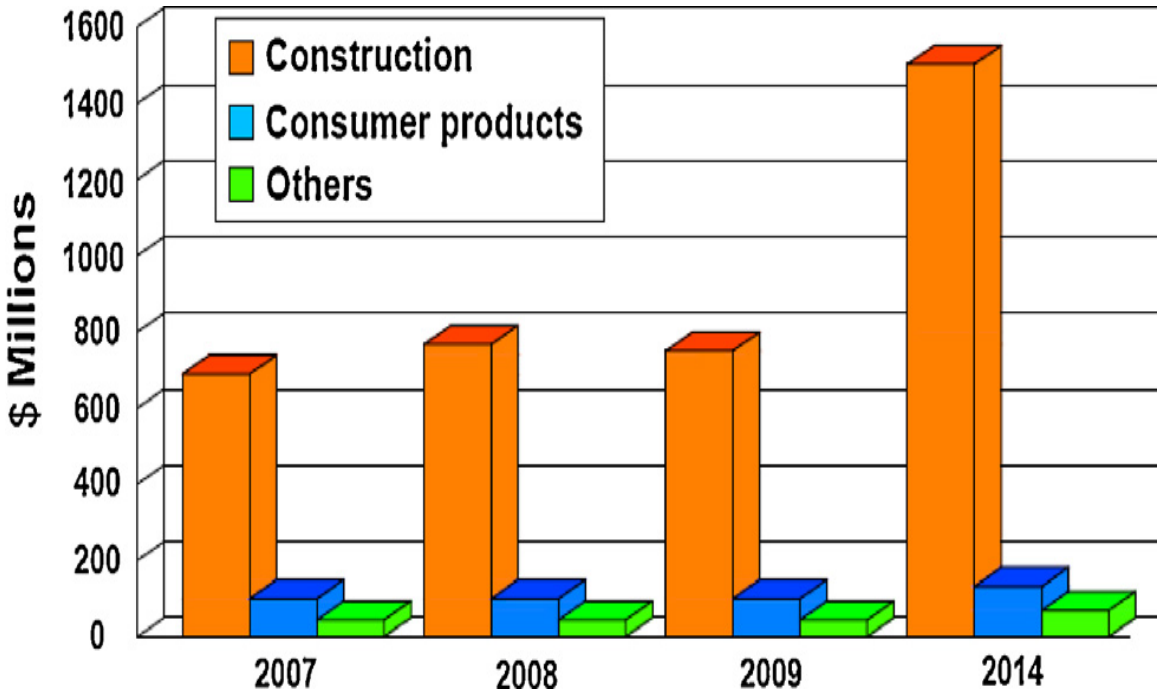

Figure 1-2.Production of photocatalyst products in the global market 2007-2014 [7].

Countless research works have been performed to determine better and efficient ways to collect solar energy to meet the increasing energy needs of the world. Photovoltaic (PV) cells are one of the common known prevalent ways to capture solar energy, but unfortunately, the efficiency is relatively low and the high cost associated with it hampers its use [8]. Another challenge is limited availability of good quality produced for traditional silicon PV cells. Solar thermal power system provides a better alternative of higher than 40% and excellent cost-effectiveness [7-8].

In the synthesis of fine chemicals and pharmaceuticals, shorter routes are often offered by a photochemical reaction in different synthetic schemes. Additionally, photocleavage (bond breaking induced by light) has also turn out to be an effective approach for the removal of protective groups [9]. The employment of photochemistry for organic reactions is however limited by the worries about scale-up and efficiency as well as safe operational processes [7-9]. Herein, an improvement in efficiency of photochemical reactions is demonstrated by the use of microfabricated reactors to enhance a continuous flow. These microreactors deliver the improved efficiency following their larger surface area. Large-scale photochemical reactions are generally accomplished with macro scale lamps dipped in the reaction vessel. In most times, it takes substantial determination to scale-up a successful small-scale reaction to its industrial equivalent [10]. The cause to scale-up of light sources, heat and mass transfer in the processes, and safety concerns are the major challenges faced by this approach (e.g. explosions caused by excess heat) [11]. Most of the photochemical reactions proceed via a free-radical mechanism. The inability of radicals formed near the light sources to diffuse rapidly may further react with other species, they are likely to recombine, which could lead the generation of excess heat instead of a

productive reaction [12]. The quantum efficiency of the overall process may be depleted or reduced as a result of radical recombination [13]. However, by miniaturization, the probability of collision of the radical species is increased by the reduction in the concentration about the light sources due to the diffusive transport of species [8-11]. A number of reaction mixtures are characterized by components (solvents or solutes) that are capable of absorbing a photon of light. In photochemical reactors designed for large scales, the magnitude of the incident light is reduced by solutions resulting to irradiations falling off the source of light, hence reducing the efficiency of the reaction unit. The success of miniaturization of photochemical reactors is associated with its high surface to volume ratio as well as the smaller scales of length employed in the fabrication of microdevices allowing thorough penetration of light into the reactor depth [14].

Following the advantages offered by miniaturization, we designed and fabricated a microreactor using quartz glass which happens to absorb below visible region. In the synthesis and analysis of fine chemicals, microfabricated reactors have faster heat and mass transfer properties resulting from dominant surface forces, high surface to volume ratio and shows laminar flow [15]. The aforementioned properties are ascribed to the micro-scaled devices with smaller lengths, which presents an advantage of microfluidic systems when photochemical reactions are carried out at this scale.

Sunlight hits the world's environment with a quality of 1367 Wm^{-2} however its energy and otherworldly appropriation is to a great extent changed by it going through the air with the wind, mists and other barometrical players' association of the extraterrestrial power, 1367 Wm^{-2} [16]. The remnant direct sunlight quality that extends to the world's surface is pretty nearly 892 Wm^{-2}. In the event that the wavelength falls beneath 300 nm, no sun-powered

photons will be recognized on the earth surface [11,13-16]. On clear climate, no adjustments in the rate conveyance in the middle of visible and infrared radiation on going through the air and in shady thick climate, the infrared radiation is favored [5].

Kingdom of Saudi Arabia is blessed with high intensity of solar light throughout the year. Sunlight is cheap, non-polluting, plentiful and limitless renewable source of clean energy. Solar energy is thought to be virtually unlimited in the long term and is a very plentiful resource in Saudi Arabia. It is a probable source of renewable energy choice that is being utilized by many countries with even low solar radiation of 3 kWh/m^2, in an effort to decrease their dependence on fossil- fuel based non-renewable energy and reduce environmental effects[16].

Saudi Arabia is situated in the middle of the world most productive solar regions, which obtains a unique type of sunlight, particularly during the summer seasons. The annual average solar radiation received on the Arabian Peninsula, in general, is about 2200 kWh/m^2 [14,16]. The geographical area between latitudes 40N and 40S in the world is referred to as Sun Belt, and Saudi Arabia falls between latitudes 31N and 17.5N which is within the range. Saudi Arabia is suitably placed in the world Sun Belt region to take advantage of solar energy. Average solar radiation in Saudi Arabia records between a maximum of 8.004 $kW/m^2/h$ at the city of Bisha and a minimum of 4.479 $kW/m^2/h$ at the city of Tabuk. The high solar radiation value >5 $kW/m^2/h$ are experienced in most parts of the country [16].

Utilization of solar energy in different ways in this part of the world is vital. Research, development, and demonstration (RD&D) activities in Saudi Arabia have established that solar energy has a lot of practical uses. Renewable energy is an essential factor that

deserves intensive research in Saudi Arabia. However, many national energy specialists in the country have worked on solar energy in the national energy policy [14].

In the near future, energy utilization needs to focus on renewable energy technologies like solar energy so that environmental impacts can be decreased.

Environmental complications are continuously growing in terms of pollutants, hazards and ecosystem degradation over broader areas. Technological advancement is also associated with dramatic change taking place in the world in many different ways [17]. However, progress and developments are associated with it. No doubt, profound environmental difficulties, and challenges accompanied with it threaten man and nature. For the last 20 years, the environmental destruction and pollution to the environment have become more obvious [18]. The increasing environmental challenges can be attributed to many factors: the number one is human activities that have increased due to the growth of world population, consumption, and industrial activities. Effluent gasses such as SO_2, NOx, particulate matters, CO, and CO_2 are another notorious environmental pollutants associated with fossil fuels and non-renewable energy [19].

The photo-oxygenation of furan derivatives has been well examined in varieties of literature, and several claims to organic synthesis have been reported. The sun has uninterrupted photon irradiation density but in minor quantities, therefore, has to be determined to achieve the anticipated high yields in petite time allowing the photoreactor itself to be kept verily small [20]. However, most photooxygenation reactions need additional illumination times associated with the huge scale experiments, it has been well

established that solar-chemical research that is carried out under non-concentrated sunlight often require some days or weeks or even months to attain maximum or ample conversion rates [14,21].

The crusade to decrease the use of expensive facilities and time-consuming reactions has been required by the prerequisite for speedy, simple operational capacities in environmental study and medical diagnostics [22]. While initial studies were directed at analytical claims, it has since been practical to synthetic chemistry in the system of the microreactor. The most exciting feature of the microreactor is the huge surface to volume ratio due to miniaturization. This gives microreactor exceptional mass and heat transfer properties as equaled to the conventional reaction vessels[23].

1.2 Solar Chemistry

Solar chemical applications have shown a significant importance which emanates from its rapid growth and development, solar chemistry has proven to be a promising trail towards achieving a long-standing goal of channeling solar energy [14]. Solar chemistry aims at obtaining utilization of sun as the major energy source to carry out photochemical reactions [24]. Any process which utilizes solar energy for photochemical reactions lies within the scope of solar chemistry. In general principle, these processes can be classified into two different categories based on how the solar radiation is utilized: Photochemical, here the reactants, sensitizers or catalyst are directly involved in the absorption of a photon of light emanating from the sun, and Thermochemical, where reactions are initiated after when the solar energy is converted into thermal energy [25].

Photochemical reactions employ the energy of photons (wavelength) absorbed from sunlight to initiate the reaction of interest. This energy is a function of its wavelength based on the equation:

$$\mathbf{E= hc/\lambda}$$

Where h = Planck's constant (6.626×10^{-34})

C= the speed of light

λ= is the wavelength

With reference to the above equation, where the energy and the wavelength exhibit an inverse relationship, any photon with a wavelength above 760nm cannot meaningfully cause an effect in the photochemical reaction owing to their lower energy [14,26]. The sunlight hitting the earth's surface constitutes nearly 4 to 5 percent in the near UV region (300-400nm), 45% in the Visible (400-760nm) and the rest in the IR and IR regions [14].

The solar photon found in the two regions UV and visible spectrum have sufficient energies for photochemical reactions to take place. The photons in the infrared regions are not important (not useful) in photochemical reactions and are mostly considered as waste heat in the process or reaction.

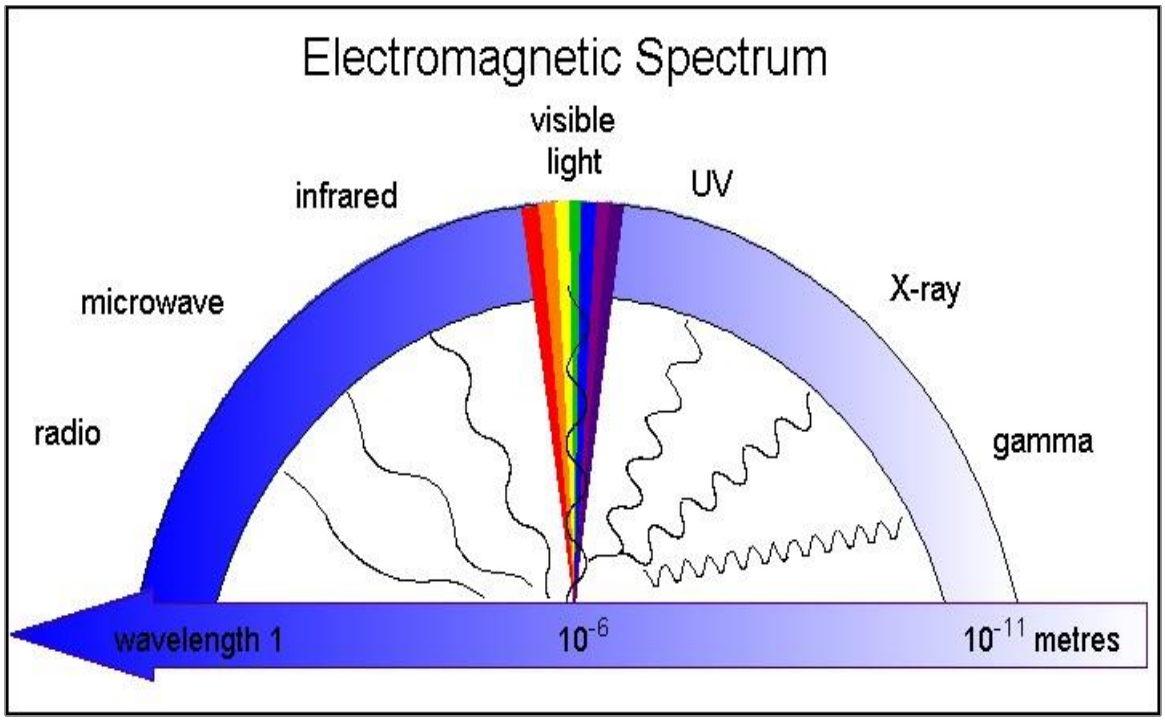

Figure 1-3. Electromagnetic spectrum

Theories of photochemistry are well known and comprehended with a wide range of synthetic transformations. The setback is the recognition of practical industrial applications which would be possible and economically viable using solar photons. Another potential approach is to use sunlight photons as a substitute for those generated from other sources, the main idea is tailored towards cost-effectiveness to initiate photochemical reactions in comparison to when reactions are driven by the use of lamps.

1.2.1 Statement of problem

The kingdom of Saudi Arabia has rich daylight and potential source to perform photoorganic chemistry as environmentally friendly power energy. Interestingly, we plan to build up a narrow stream reactor for the examination of "green organic synthesis" utilizing organic dye as a catalyst [16]. Utilization of stream reactor has a few points of interest, for example, effectively scale up the creation of products in extensive amounts.

As of late, various written works were accounted for on the utilization of metal complex photograph redox catalyst that utilizes low power visible light illuminated source [27]. However, the utilization of metal complexes is harmful and very expensive, hence, the development of UV light-induced reactions is highly desired and promising most especially under metal-free conditions. Organic dyes, which are more environmentally friendly, cheaper and easier to prepare, present a feasible alternative to inorganic photocatalysts in organic synthesis and the advancement promising especially under metal-free metal conditions [28].

1.2.2 Significance of study

In this work, we will explore some organic reactions using a continuous capillary flow reactor and dye as catalyst (metal-free) under sunlight irradiation. This will help create a new direction in photochemical reactions to investigate reaction products.

1.3 Research objectives

1 To fabricate a continuous capillary flow reactor

2 To optimize the reaction conditions with different organic dyes under sunlight irradiation.

3 To employ the capillary microreactor to examine the efficiency with regards reactions yield using sunlight compared to other light sources as reported in literature.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

During the previous two decades, the development and application of novel technologies focused on decreasing environmental pollution significantly improved in all research areas [29]. Organic chemistry is one of the major hazardous waste manufacturers as it forms the basis for a variety of products including pharmaceuticals, cosmetics, and surfactants as well as agricultural products. It is expected that for every 1 kg of active products of pharmaceuticals, a range of waste ranging from 25 and 100 kg are generated [30].

Furthermore, every single large-scale industrial process consumes enormous amounts of energy as well as fossil fuels. As a result, the chemical industry is encountering a serious challenge in this regard. In order to stay on track, a sharp decline in pollutant and greenhouse gasses emitted at every point in time must occur without affecting the markets for its products [31]. In order to attain this height, new measures have to be employed to change both the approach and the technology used throughout the production processes. For this reason, microtechnology has acknowledged a great deal of interest. Microtechnology application has shown a rapid growth in many areas like electronics and engineering. The development of microstructured devices employed for chemical reactions was newly embraced within last decade.

Scaling down of chemical reactors offers numerous principal and useful favorable circumstances of pertinence to the pharmaceutical and fine chemical industry [32]. The industries are always scanning for controllable, data rich, high throughput and naturally sufficient strategies for creating products with a high level of synthetic selectivity. Without an iota of doubt, for pharmaceutical organizations and informatics-based methodology, that microreactor chemistry can remarkably convey, may be the trigger for a stage change in procedures [14, 16, 18-28].

This study investigates how scaling down may alter photochemical synthesis, as a novel chemical innovation and procedure in which the responses, for the most part, delivers the desired products in higher yield and virtue, in shorter stretches of time, compared with the conventional batch reactions. Also, the execution of photoreactions in small scale reactors is along these lines highlighted with regard to their ecological criticalness contrasted with the traditional systems.

2.1.1 Microphotochemistry

Microphotochemistry is a novel exploration area of the 21st century that emerges from remarkable advancement in chemical synthesis taking into account miniaturized scale and nanotechnologies. Enthusiasm for scaling down expanded in every aspect of science, technology, and engineering because of the general propensity for greener modern and scholarly research forms. Along these lines, 'molecular microreactor', for example, nanoparticles, zeolites, dendrimers, capsules, and micelles discovered across the broad application in the screening of medications and pharmacokinetic examinations of bioactive compounds [12-13]. In chemistry, scaling down is particularly connected to the

explanatory terms "Lab-on-a-chip" and "Small scale Absolute Analytical Systems" [34]. Microphotochemistry consolidates built up systems in natural photochemistry and constant stream microsystem designing with advances in LED Technologies [35] as shown in Figure 2-1 below.

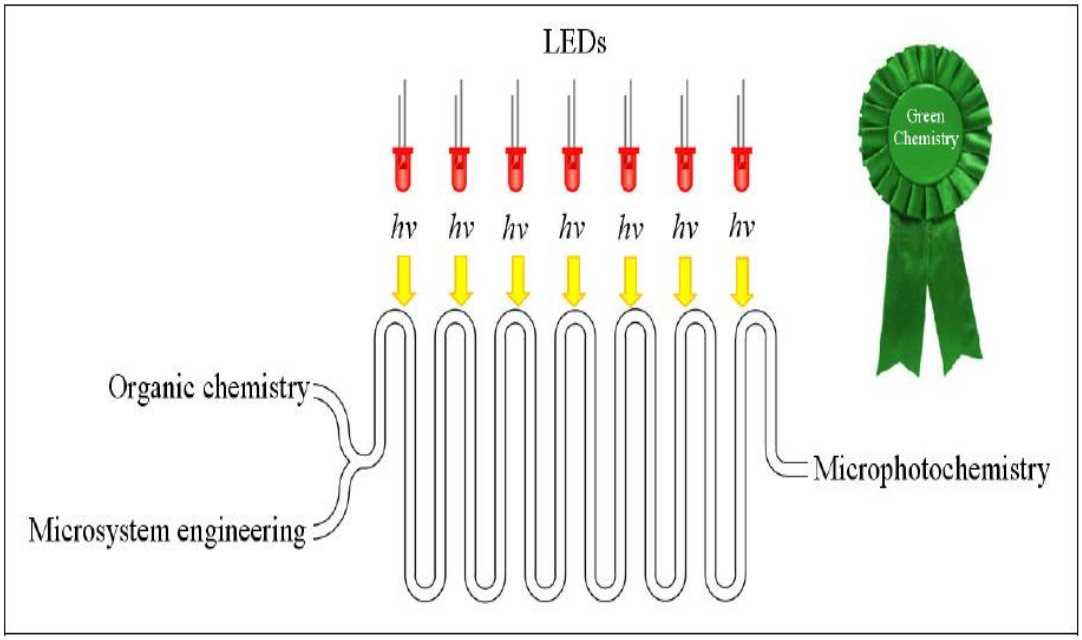

Figure 2-1 The concept of micro photochemistry - organic chemistry meets microsystem engineering.

Micro-photochemistry as a multidisciplinary subject is an essential device for some process sciences. It opens new asset and energy effective methodologies in synthetic science. In the design of microreactors, photochemical procedures are utilized as model responses to improve operational configuration. An imperative utilization of the LED-based smaller scale photoreactor innovation is conceived in the modern way of R&D practices, specifically inside of the pharmaceutical industries. The gadget is little, asset effective, simple to work and ought to act as per all cGMP-rules (current great assembling practice) [36].

As of late, multiple fields of study research became increasingly crucial and photochemistry turned into a flawless case as a capable scaffold between sciences as a whole.

2.1.2 Principles of photochemistry

As indicated by the IUPAC proposals published by J. W. Verhoeven in 1996 [37], photochemistry is "the branch of chemistry concerned with the chemical impacts of light"; it considers chemical reactions, isomerization and physical conduct that may happen by the effect of electromagnetic radiation.

Two major standards shape the premise of comprehensive photochemical changes:

•The first law of photochemistry, the Grotthuss-Draper law, [14] expresses that light must be consumed by a compound for a photochemical reaction to occur.

•The second law of photochemistry, the Stark-Einstein law or "photoequivalence law" expresses that for every photon of light consumed by a chemical system, one particle is initiated for consequent reaction [14].

Typically, a reaction happens when a molecule picks up the vital activation energy to undergo changes. On account of photochemical reaction, light gives this energy. Max Planck hypothesized that energy is moved in parts known as quanta and equivalent to ***hv*** [13]. The interaction of a substrate molecule with light, where S_o is the ground state and S* is the excited state of the atom, can be seen as shown below.

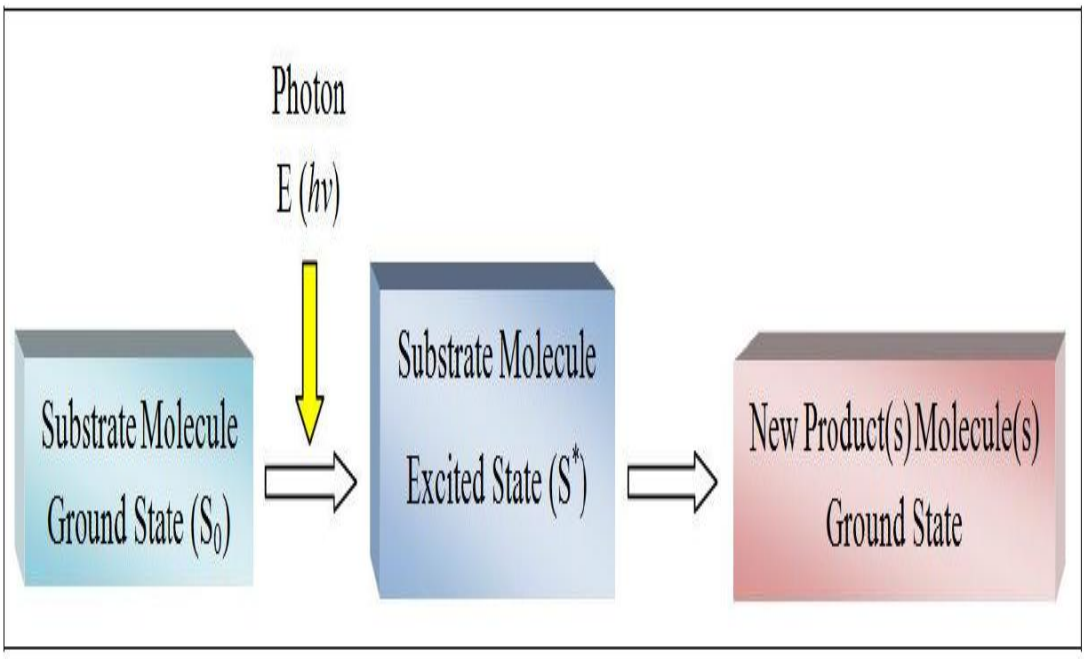

Figure 2-2. Electronic states in photochemical reactions

Absorption of visible and UV light in a molecule presents energy adequate enough to break covalent bonds. From the correlation **E = hc /λ,** it is clear that the longer wavelength visible light is greater than the shorter wavelength (200 to 400 nm) and close to the UV regions (628 to 293 kJ/mol). Subsequently, UV light is regularly used to incite photochemical reactions [38].

A molecule is in its ground state (S_o, singlet state) before photon absorption, after photoexcitation the molecule is raised to a state of higher energy, an excited singlet state (S_1), or after intersystem crossing (ISC) or a triplet state (T_1), that is followed by electronic configuration changes. In the excited singlet states, the electron spins are matched, although in the triplet excited state it is parallel [39].

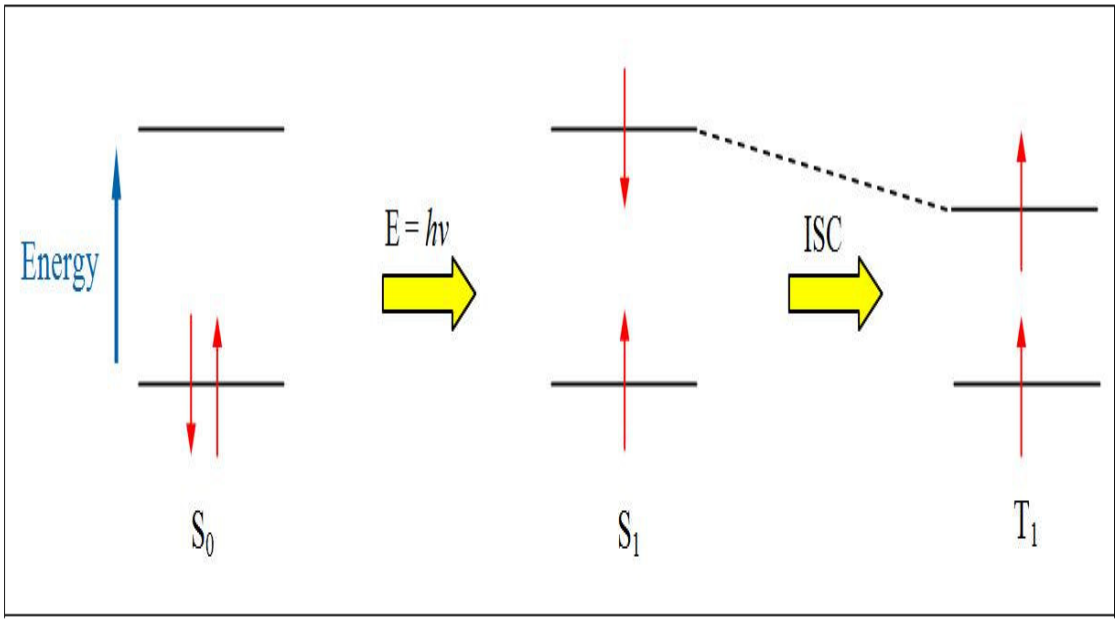

Figure 2-3. Singlet and Triplet excited states.

Once excitation has occurred, there are several number of paths which are important in the deactivation of the excited states· The Jablonski diagram presented below in Figure 2-4 exemplifies a few of these progressions:

1. Radiation of light and return to the ground state; If the photon emission transpires amongst states of identical spin state (*e.g.* $S_1 \rightarrow S_0$) this is called fluorescence. If the spin states of the initial and final energy levels are dissimilar (*e.g.* $T_1 \rightarrow S_0$), the emission is called phosphorescence. Phosphorescence takes place at a longer wavelength (lower energy). The lifespans of fluorescent states are very little (1×10^{-6} to 10^{-9} seconds), however, those of phosphorescence are meaningfully longer (1×10^{-3} s to minutes or even hours) [18-20].

2. Non-radiative deactivation; There are three substantial radiationless deactivation routes: Internal conversion (IC), Intersystem crossing (ISC) as well as vibrational relaxation (VR). IC is a non-radiative transition among energy states of the identical spin state (analogous with fluorescence as per radiative process). The aforementioned processes take place swiftly with the loss of heat (1×10^{-11} to 10^{-14} seconds). Intersystem crossing is a radiationless transition among dissimilar spin states (analogous to phosphorescence) [14, 16-20]. The ISC is slower than internal conversion (1×10^{-6} to 10^{-11} seconds). Intersystem crossing permits the excited singlet state to extend to the lower energy triplet state by spin inversion. By means of this mechanism, a triplet state can be occupied indirectly. The lifespan of the triplet state is typically high as $T_1 \rightarrow S_0$ is forbidden [40]. Vibrational relaxation is the most common of the three non-radiative deactivation routes. It regularly happens very swiftly (1×10^{-10} to 10^{-12} seconds) and conveys the molecule into the novel energy minimum structure for the excited state [40].

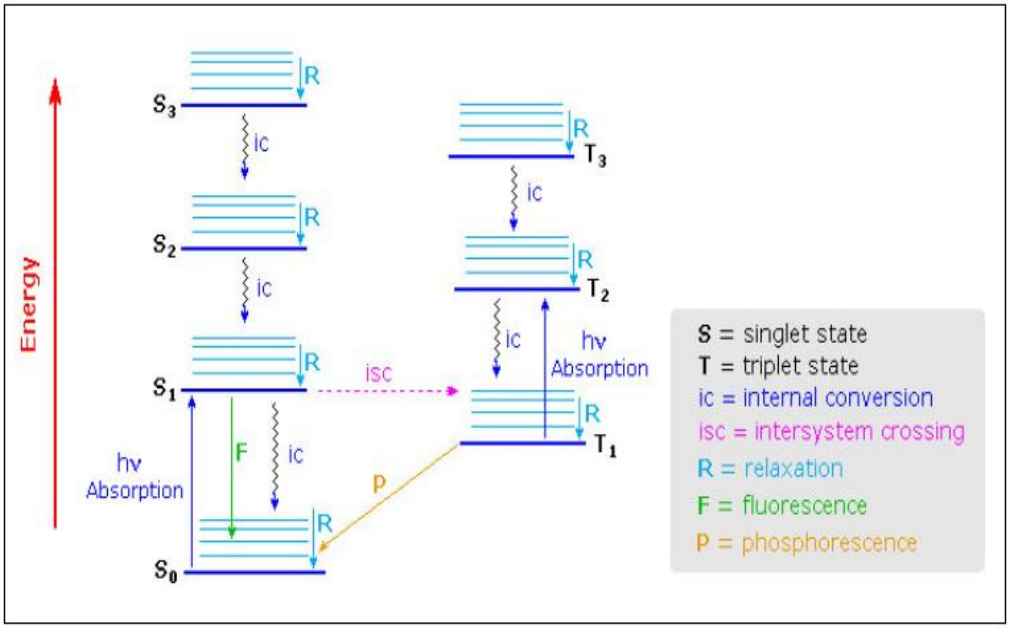

Figure 2-4. A simple Jablonski diagram.

3. Quenching of the excited state; Energy is transmitted to a different molecule in the way of vibrations or rotations. This happens through the collision of an excited molecule with another ‘particle' in the reaction media [41]. The core quenching factor in liquid samples is solvent molecules. This outcome could be abridged in photochemical transformations where acetone is utilized as both solvent and sensitizer. "Quenching" is a very vital route for photochemical reactions when intersystem crossing of the substrate is ineffective [9]. In this situation, the realization of the substrate triplet excited state is probable via transmission of energy from an upper triplet excited state of an appropriate sensitizer (catalyst) molecule [42]. This collisional process is called triplet sensitization and opens an incidental route for $S_0 \rightarrow T_1$. The triplet energy of the sensitizer (donor) need be greater than that of the substrate (acceptor), i.e. E (Z) > E (M). Spin upkeep necessitates spin interchange to take place throughout the collisional energy transmission [43]. Therefore, a sensitizer triplet (Z_T), produced from sensitizer molecule (Z_0), reacts through a ground state substrate molecule (M_0) as presented in Figure 2-5 below. The perfect sensitizer (Z) absorbs light favorably thru reverence to the substrate (M) and go with effective intersystem crossing to a triplet excited state (T_1) [15-19]. This robust state then aids to trigger a substrate molecule to a trivial energy triplet state by collisional exothermic energy and spin interchange, returning the sensitizer to its ground state.

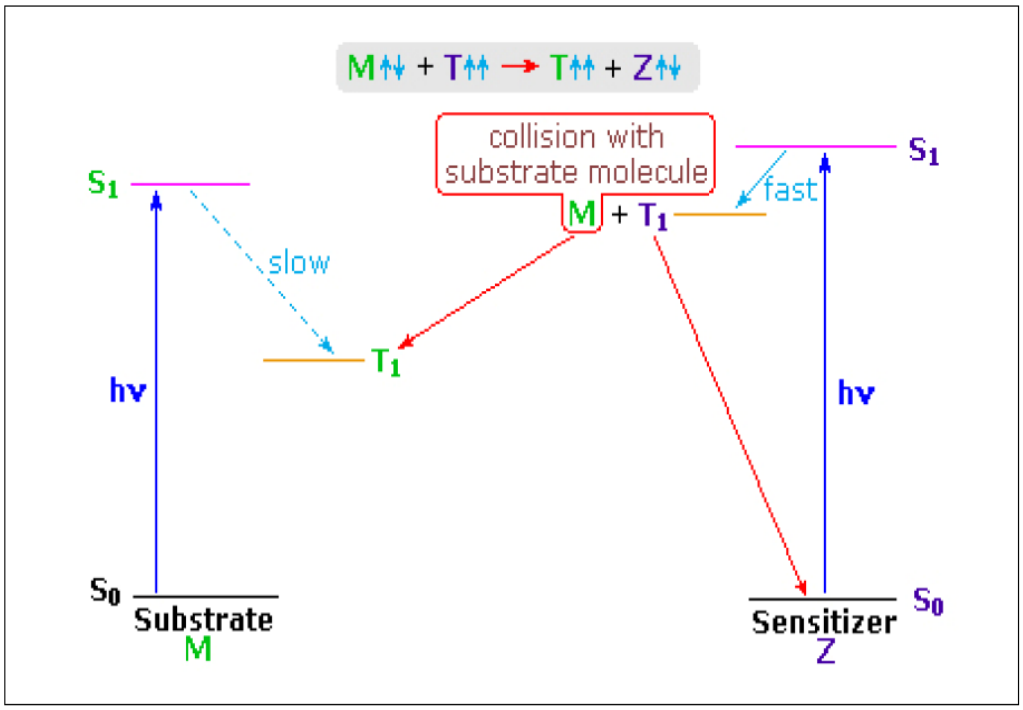

Figure 2-5 Triplet state sensitization process

Photochemical reactions without the addition of any reagents, substrate activation usually occurs, which reduces by-products formation [44]. In many literature photo-oxygenation of furan derivatives has been well studied, and several applications to organic synthesis have also been examined [45]. The sun has continuous photon irradiation density but in smaller quantities hence has to be concentrated to achieve the desired high yields in short time permitting the photoreactor itself to be kept verily small [46]. Though most photooxygenation reactions need more illumination times compared to the large scale experiments, it has to be considered that solar-chemical experiments that are carried out under non-concentrated sunlight often require several days or weeks or even months to reach high or complete conversion [34, 35, 41-44].

Figure 2-6. Shows a setup under concentrated sunlight used for photo organic reactions [12].

The quest to reduction has been compelled by the need for quick, simple on-line measurements in environmental analysis and medical diagnostics. While initial studies were targeted at analytical applications, it has since been applied to synthetic chemistry in the form of microreactor [47]. Interestingly, microreactor has a large surface to volume ratio due to miniaturization which gives it excellent mass and heat transfer properties as compared to the conventional reaction vessels, thus allowing improved temperature control and eliminating the risk of explosion [48]. Reactions can, therefore, be carried out under more aggressive conditions. The large increase of surface area in the microreactor is also beneficial for surface-catalysed reactions [49]. Hence, reactions can be conducted at room temperature. Compared to conventional synthesis, the high degree of temperature control and high mixing efficiency in the microreactor also reduce side-reactions and prevent thermal decomposition, leading to higher yield, selectivity and purity under shorter time frame [50]. Microreactor also requires fewer reagents and produces less waste. This is cost efficient, safer and beneficial to the environment [51].

By connecting multiple microreactors, it is possible to prepare the exact amount of the chemical reagents required at the point of usage [52]. This minimizes the need to transport and store hazardous or unstable material. It is also possible to scale up production by repeating the same microreactor unit, thus enabling a cost-effective commercial production [53].

Microstructured reactors, recently have become an essential topic in industrial chemistry. The technique is normally important for the examination of fast or highly exothermic reactions assisting isothermic reaction conduction and in the process reducing the

formation of by-products and also increases safety [54]. Several photochemical reactions can be found among a large number of processes already performed in these reactors.

Continuous flow reactors are a fast growing field and have high priority to transform the ways synthetic chemistry is conducted in both industrial and research levels unlike batch reactor technology, which has little improvement in the last century [14, 19-27]. Compared to stirred tank reactors, flow reactors have more advantages like improved thermal management, mixing control and the application of extreme reaction conditions. Consequently, the reaction temperature can be maintained and controlled while reducing the volume of solvent employed [55]. In addition to heat and mass transfer, efficient mixing as well as high precision, continuous flow reactors are generally smaller than batch reactors [56].

2.2 Types of microreactors

Most of the microreactors have fairly simple designs which are made up of microchannel network mostly entrenched in a solid base [57]. On a general basis, the reactor designs are often dependent on the nature of application which is identified by some factors. The major concern in reactor design is made by considering both physical and chemical properties of the material employed for the design and both the solvent and reagents used for the application [58]. The fabrication of microreactors emanates from a range of materials such as ceramics, polymers, stainless, steel, glass and silicon.

2.2.1 Glass microreactors

The glass is considered the best type of material in photochemistry since it poses the benefit of light transparency [59]. Furthermore, the progress of the reaction can be made visual

and it is inert chemically to most of the solvents and chemical used in the concept. Various types of glass materials have been known and used in the laboratories. The choice of glass to be chosen place its fate on the reaction conditions and on the spectral emission of the source of light since glass performs the task of cut-off filter [60]. Different type of glass material has distinct light transparency for example.

Quartz λ > 200nm

Vycor λ > 220nm

Foturan λ > 280nm

Pyrex λ > 280-300nm

Soda lime λ > 320nm

Borosilicate λ > 350nm.

However, the major and most common of all the glass types used in photochemistry are the Quartz and Pyrex.

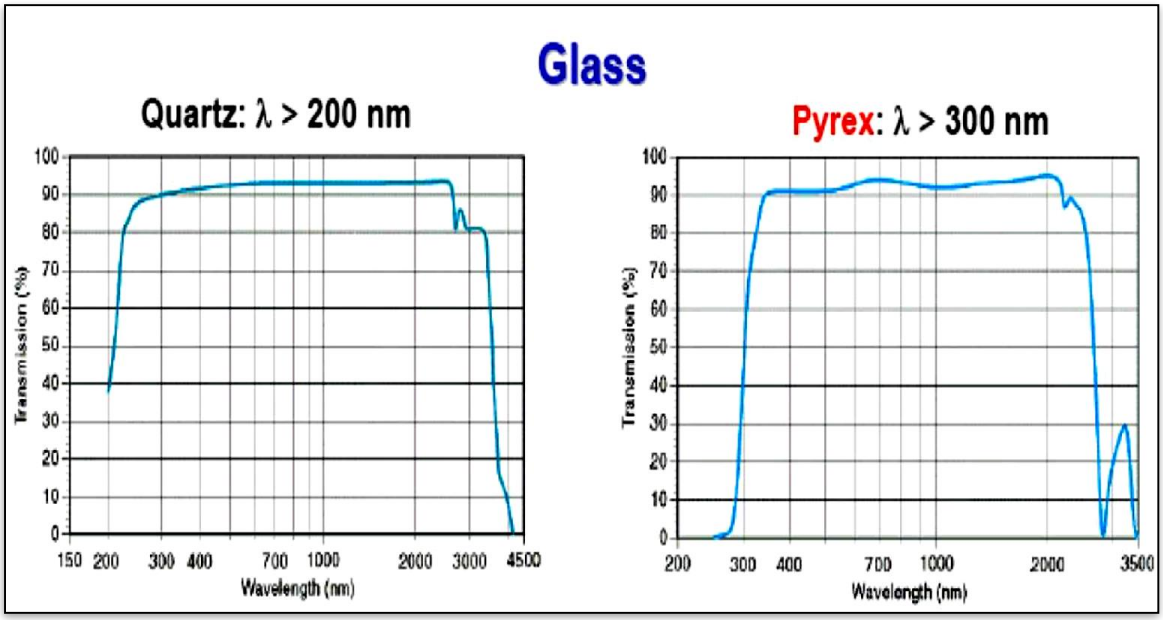

Figure 2-7. Transmission spectra of Quartz and Pyrex Glass [61].

2.2.2 Stainless steel microreactor

This also is another material used in process chemistry. These reactors found their significant attention in the fine chemical application and hence for the pilot plant, this type of reactors are rarely or not even applicable in academic laboratories because of their cost [62].

2.2.3 Silicon microreactors

These types of reactors are of interest in the fabrication of microreactors following it's behavioral (glassy) after oxidation and chemically resistance to most solvents [63]. The main purpose of its use in these areas is due to its exceptional thermal conductivity. Hence, microreactors fabricated from silicon have very good heat transfer competencies and are desirable for exothermal reactions and those that involve varying temperatures [64]. More so, the reactors can be fabricated alongside incorporating silicon-based microsensors.

2.2.4 Ceramic microreactors

The usage of ceramic in microsystem reactors has been of historic and more unusual than the use of other materials in reactor fabrication [65]. It is very difficult to fabricate microreactors using ceramic, this also relates to their limitations to operation in high-temperature applications [66].

2.3 Accessible sources of light used for photochemical reactions

The product of photochemical reactions is an outcome of the absorption of light and is dependent on the specific excited state species resulting from irradiation [67]. Therefore, the product generated from the photochemical reaction is the aftermath of the properties of

light used to initiate the reaction of interest [68].In summary, a variety of light sources used for both micro and batch photochemistry has been reported in literature [69].

Below are some examples of artificial sources of light used in laboratory scale reactions for continuous irradiation:

- ✓ Electric discharge lamps such as Hg lamps, Xe etc.
- ✓ Incandescent lamps
- ✓ Resonance Lamps (e.g Cd,Xe,Zn,Na)
- ✓ Rayonet Lamps
- ✓ Excimer Lamps
- ✓ Lasers
- ✓ LEDs and OLEDs (light emitting diodes)

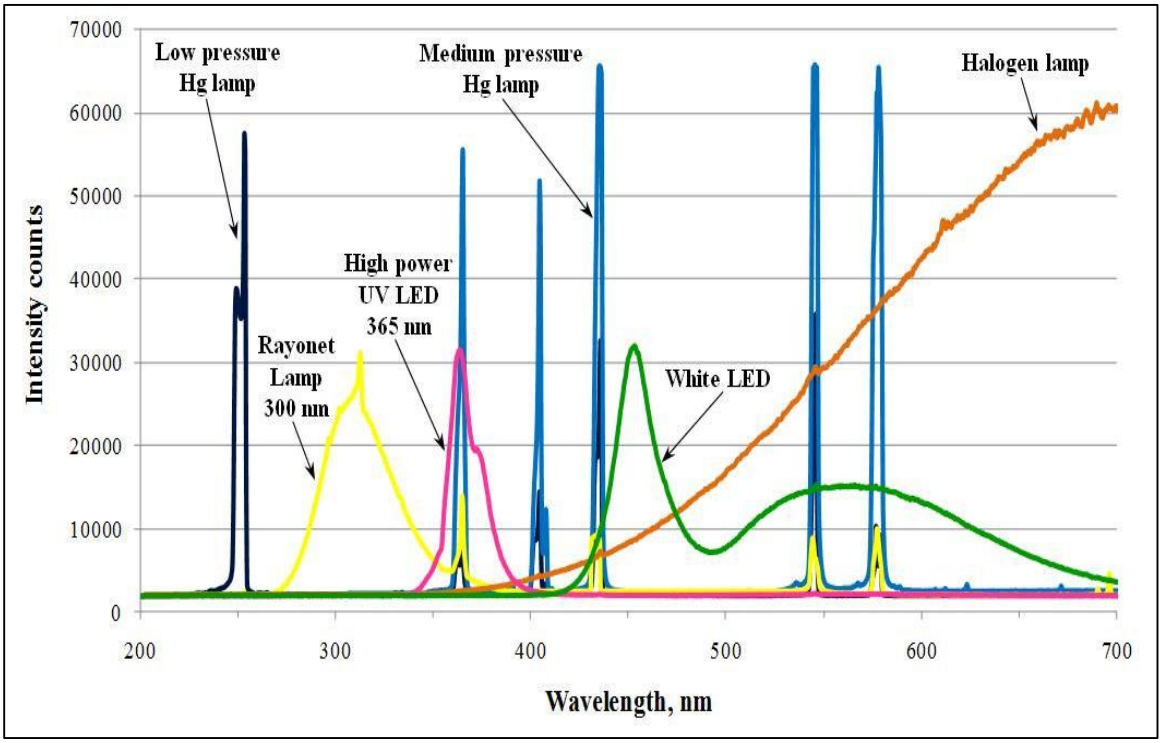

Figure 2-8. Spectra of some light sources.

Figure 2-8 above shows the features of emission spectra of major artificial sources.

As the scope of this work is concerned we will only talk about the LEDs as an artificial light source amongst the list highlighted above, which seems to be the most prominently used in laboratory photochemistry.

2.3.1 Light emitting diode (LED)

LEDs (light emitting diodes) are semiconductor source of light that are employed in photochemical reactions in the recent age [70]. They seem to be the most often used source of light in the photochemistry of microreactors following their size and the efficiency in their output. A typical LED is less than 1 mm^2, with components made easy for shaping radiation pattern [71].

Aside the disadvantages of cost and extended reaction time posed by LEDs, the following are some benefits derived from using LEDs;

- ✓ Longer lifespan
- ✓ Highly robust
- ✓ Small in size
- ✓ Swift switching
- ✓ Highly durable and reliable
- ✓ Hg free and safe mode of operation
- ✓ Lower energy consumption.

The high power LEDs having their emission in the visible range are lower in cost unlike the UV-based LEDs which currently record high cost which limits their use in applications

[72]. Hence, LEDs are often used as a source of light in the photochemical reaction for irradiation and for a quantifiable experiment such as quantum yield measurement [73].

2.4 Photocatalyzed organic reactions

Some organic reactions catalyzed by different sensitizers both organic and inorganic under solar irradiation which have been reported in literature.

Rueping et al. [74] a work on C-H functionalization of tertiary amines using rose Bengal as a sensitizer, N-phenyltetrahydroisoquinoline with nitromethane as a nucleophile source and were able to isolate 92% of the desired product with optimized reaction conditions. The reaction took around 5hours under green LEDs irradiation.

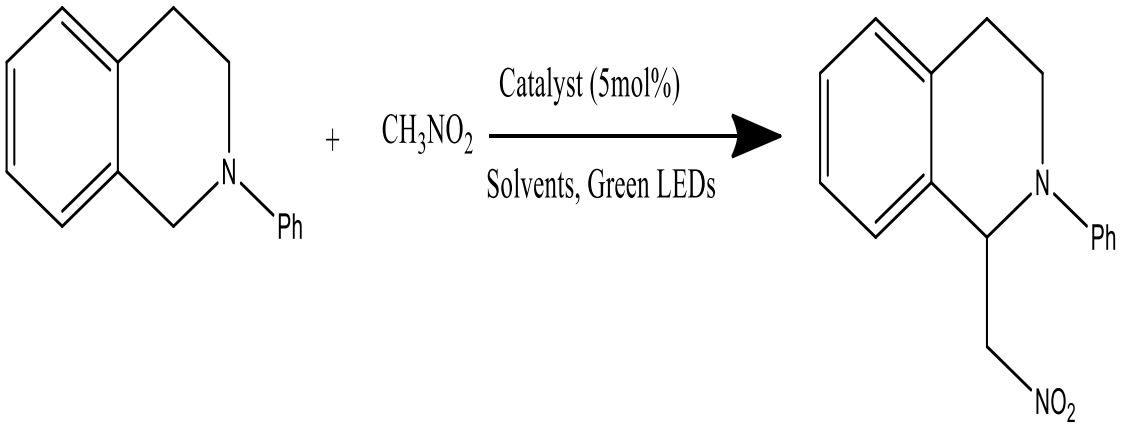

Figure2-9. Dehydrogenative coupling reaction using tetrahydroisoquinoline derivative [75].

In the same work of Rueping et al. [75] they carried out some reactions using N,N-dimethylaniline as their amine substrate with different isocyanides in the Ugi-multicomponent reaction in flow and were able to recover good yield of the desired products.

Based on our literature search, we came across the following photochemical reactions which were basically monitored under sunlight irradiation unlike the famous and known LED light sources [76]. Below are some examples of Tetrabutylammonium decatungstae (TBADT) Photocatalyzed functionalization of electrophilic olefins upon to solar irradiation.

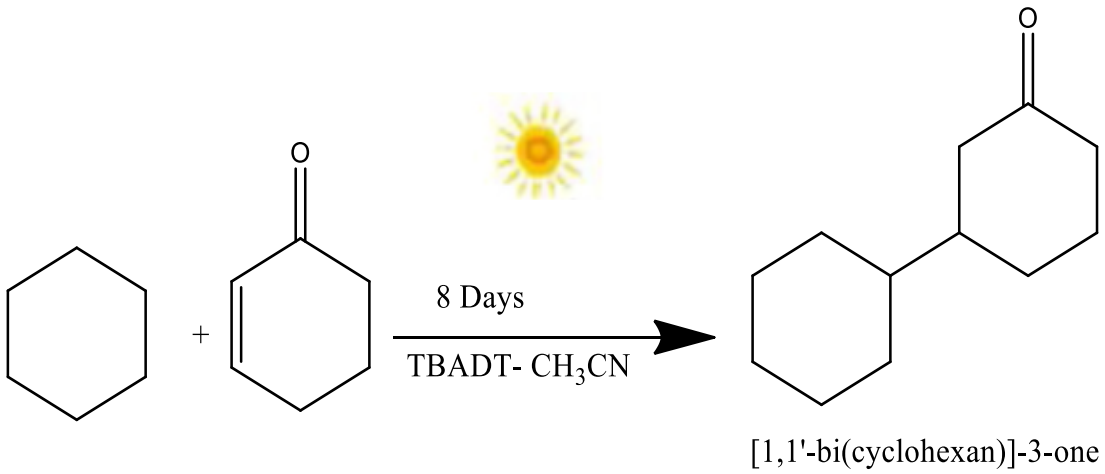

Figure2-10. Reaction of cyclohexane with cyclohexenone with Tetrabutylammonium decatungstate TBADT as a sensitizer. 40% yield [77]

Figure 2-11. The reaction of cyclohexane with cyclohexenone with Tetrabutylammonium decatungstae TBADT as a sensitizer. 40% yield [77]

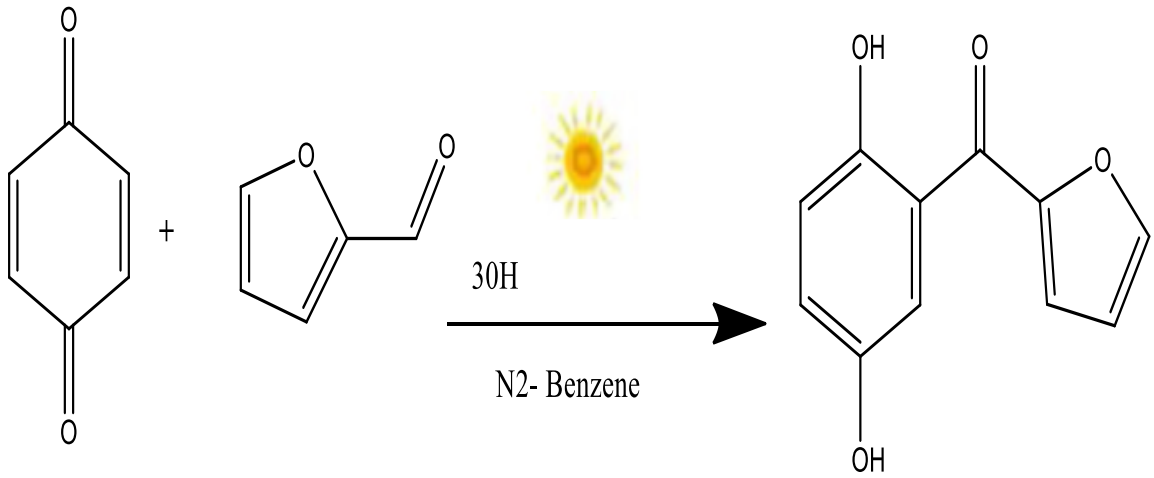

Figure2-12. The reaction of a Quinone with an aldehyde (furfural). 88% yield [78].

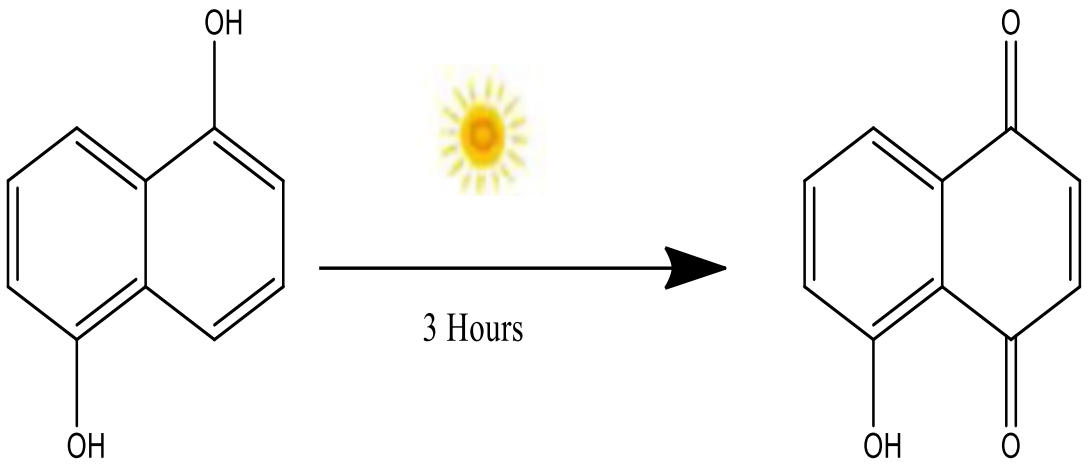

Figure2-13. Production of juglone from 1,5-dihydroxynaphthalene 57.5% yield [79].

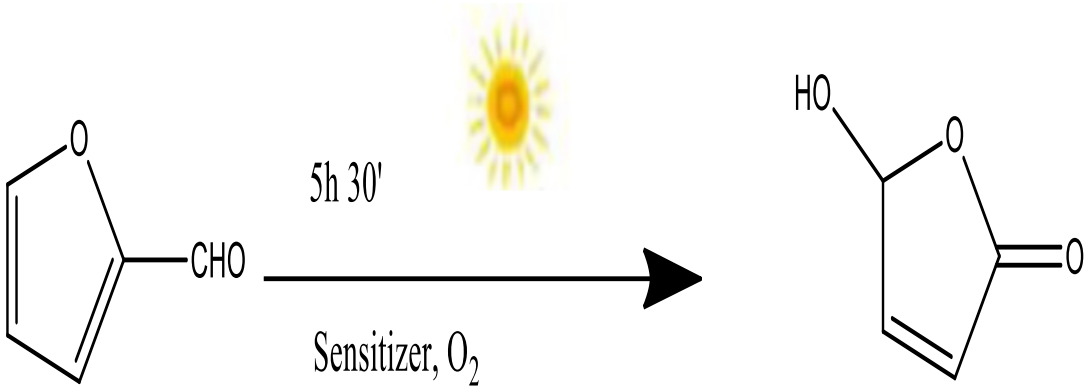

Figure 2-14. Acetalization of 5-hydroxyfuran-2[5H]-one in methanol to give methoxyfuran-2[5H]. 69-94% yield [73].

All the aforementioned reactions were irradiated under sunlight in the absence of a microreactor. The incorporation of microreactors in a continuous fashion could increase the reaction rate by decreasing reaction time.

More so, Yuanhang Pan and his team [80] carried out dehydrogenative coupling reaction using 4-methyl,N,N-dimethylaniline under LED irradiation and were able to isolate 48% of the desired product in about 96hours. Afterward, they performed the same reaction under the same LED source using N-aryltetrahydroisoquinoline which is a cyclic amine and more reactive than the former, they were able to isolate about 92% of the product in just 20hours. In their final analysis, they carried out the later reaction under sunlight irradiation and they isolated 87% of the product in just 3 hours of reaction time.

Rueping et al. [75] were first to apply an acyclic amine for the cyanation reaction. In their work, the used an iridium complex as a catalyst together with acetic acid as cocatalyst. The reaction was irradiated under the 5W fluorescent bulb. The reaction took about 12-96h before completion and yield were about 82%.

Pan et al. [80] in their work employed a cyclic amine for the cyanation reaction using RB, graphene oxide as cocatalyst. The reaction was irradiated under green LEDs, a yield of 96% was achieved after 30h of reaction. However, in addition to availability and cheapness, reactions irradiated under sunlight tends to be faster compared to the conventional LED approaches of the light source for reactions.

Lorna et al. [81] in their study reported the photoacylation of naphthoquinones to be very slow in sunlight irradiation in regions with higher latitude. They carried out their reaction after successfully optimizing the reaction conditions such as that reported by Benites et al.

[82] who used benzene as the solvent media for the reaction. Instead, they used trifluorotoluene, a less hazardous solvent, and a faster reaction was achieved under a solar simulated light source. The achieved the corresponding product in excellent yields (17-81%).

Subsequently, Schiel and his coworkers [83] in their study carried out the reaction using a more environmentally friendly mixture of solvents (t-butanol-acetone) under sunlight irradiation. Nevertheless, they were unsuccessful due to the complex set up the requirement to capture and focus sunlight on the system. Success was achieved with excellent yields under sunlight irradiation when Benites et al. [82] carried out the reaction in regions of lower latitude, however benzene was chosen as the solvent media for the system.

Herein, we carried out this reaction in Dhahran Saudi Arabia. Saudi Arabia is known for its high sunlight intensity around 2200kW/m^2 with some part of the kingdom experiencing about >5kWh/m^2/day [16]. An example is Dhahran where the reaction was conducted. Solar/sunlight chemistry is an important area of photochemistry that emphases on the instigation of photochemical reactions by means of solar radiation [84]. In this fashion, it is reflected to be an additional step in the direction of "green" chemistry as it abolishes the need for energy challenging lamps (halogen, Hg, and Xe) and substitutes them with an alternative renewable means, SOLAR RADIATION [85]. although, a functional area of photochemistry, the research area of solar chemistry has developed swiftly in the recent years [86]. In place of a direct result of this augmented level of attention and research, a great quantity of solar technology has been established to capture and utilize the sun's rays for a wide range of applications [87]. These applications vary from photovoltaic solar

panels aimed at power generation, water heating systems and waste water handling methods to chemical synthesis tools [88].

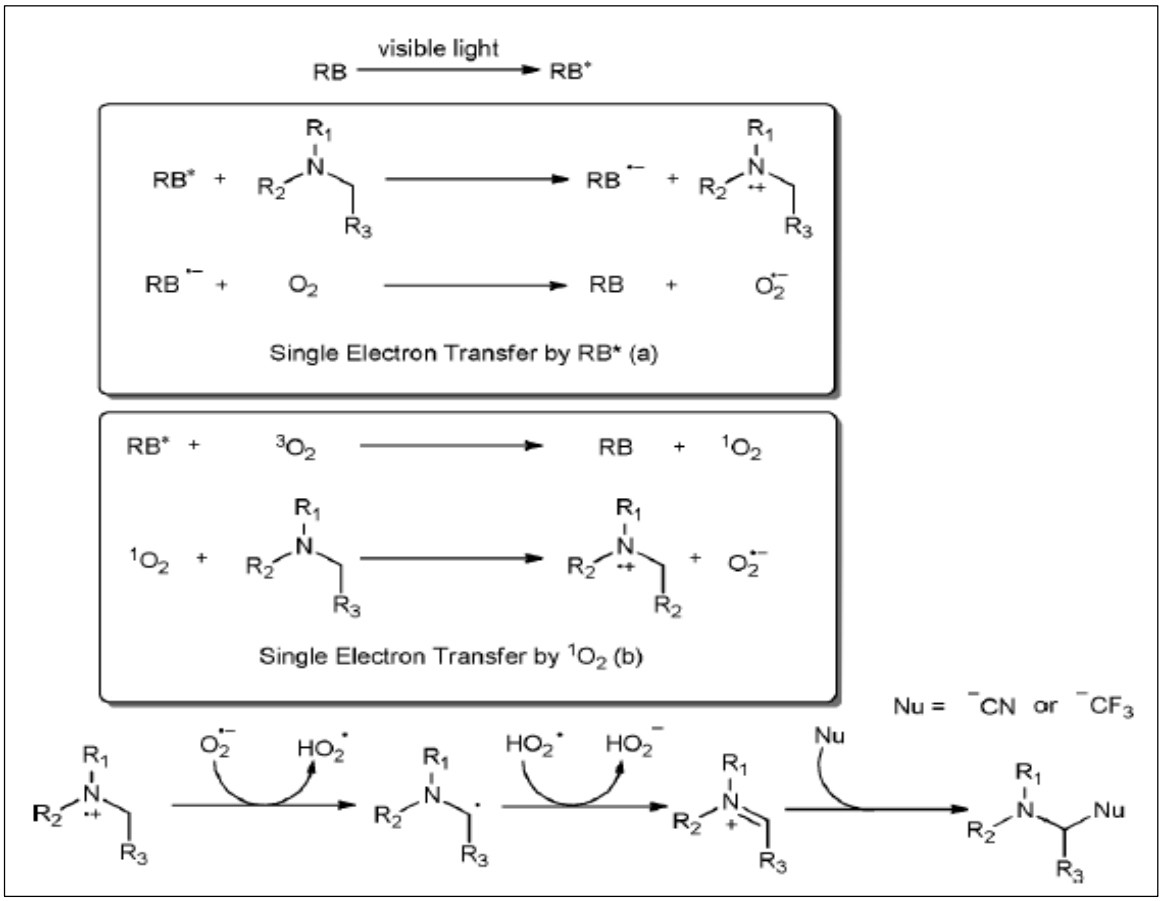

Figure 2-15. Proposed mechanism for α-Functionalization of tertiary amines [80].

Pan et al. [81] proposed the above mechanistic path that an absorption of a photon of light by RB from the light source gets it excited to RB* and takes a single electron from the Nitrogen atom in the tertiary amine through an SET process (Single electron transfer). The system is completed by reoxidation of the $RB^{*\cdot}$ anion radical back to the ground state again RB by molecular O_2. The tertiary amine generated is acidic and further deprotonated by a very strong base $O_2^{\cdot -}$. This species produced is highly reductive and a second SET takes place by another oxidation of the carbon radical generated in the substrate, hence forming a highly reactive iminium intermediate which is simply attacked by an incoming nucleophile to produce the desired product of α-aminonitrile.

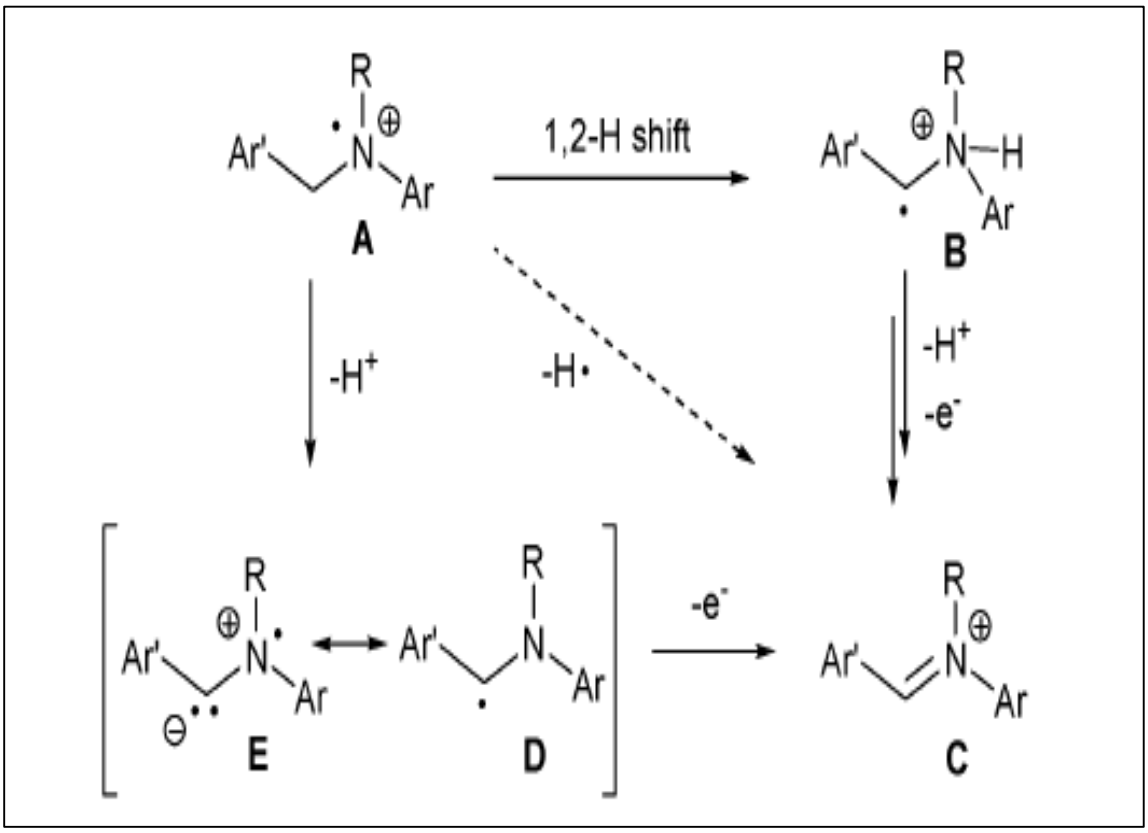

Figure 2-16. Mechanism of iminium ion formation [75]

The mechanism of the reaction was described by Rueping et al [75]. they suggested a different path to form the iminium intermediate which contrasts previous mechanism described by Pan et al [81]. Once the RB is excited after absorption of a photon of light, the tertiary amine transfers a single electron to the dye which quenches it back to the ground state and becomes a radical. The amine radical undergoes a 1,2-H shift to generate a carbon centered radical which is deprotonated by the super peroxide anion to form the iminium intermediate [75].

The first scenario “in cage” was first proposed by schenck which was established beyond by Maruyama et al. [89], proposes the generation of a “caged biradical triplet which couples directly to produce the corresponding product of acylation. Alternatively, the scenario of the “out cage”, as initially suggested by Moore [90] which was subsequently strengthened by Bruce [91-93].

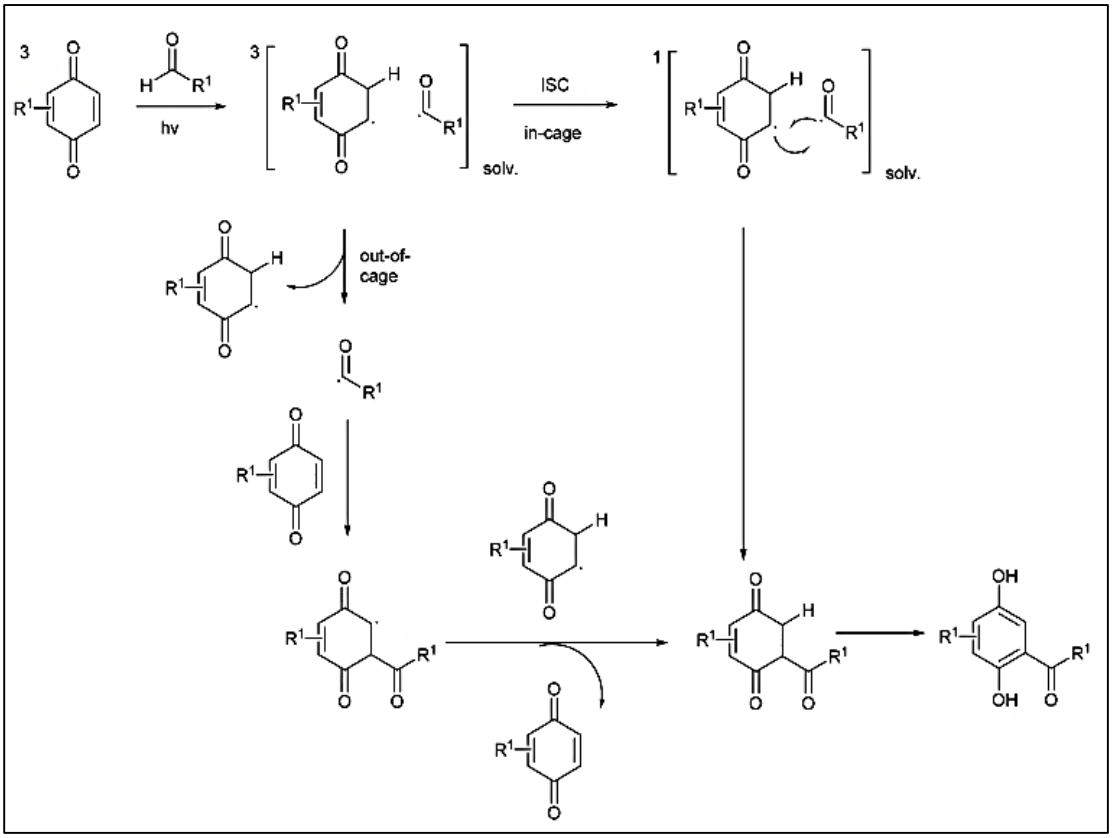

Figure 2-17. Proposed mechanism for Photoacylation reaction of naphthoquinones

CHAPTER 3

RESEARCH METHODOLOGY

3.1 Solvents, Chemicals, and Reagents

Rose Bengal (≥90%) was purchased from Sigma-Aldrich. Acetonitrile (UHPLC Super grade 99.9%) was purchased from Panreac AppliChem Company, Fluorescein dye, Nitroethane (≥95%) from Fluka, Eosin Y (88%) dye content from Fisher certified biological stains. KCN (97+%) was purchased from Alfa Ascar, Acetic acid (> 99.5%) from Fluka Chemica, Ethyl acetate (99.9%) was purchased from Analar Normapur and Hexane (99+%) was purchased from Sigma-Aldrich. All the solutions were prepared with deionized water (Siemens Ultra-clear, Saudi Arabia).

3.2 Materials

All glassware used in this experiments were properly cleaned with deionised water from Siemens Ultra-Clear water purification and finally rinsed with the solvent of interest then oven-dried at least 1hr before use.

3.2.1 Reactor design and fabrication

Following the advantages of continuous flow methods over the traditional batch reaction, high interest has been shown in this approach. Some of the advantages include; reproducibility, control of reaction parameters with precision, efficient energy and ease to scale-up reactions. In this regard, the efficient conversion may be constrained due to uneven light penetration through the system. In essence, we designed and fabricated a

capillary flow microreactor for an efficient continuous flow using a commercially available glass material, quartz.

In this work, we fabricated three types of capillary reactors for the purpose of enhancing the formation of desired products in reduced reaction time due to higher volume to surface area as a result of miniaturization.

3.2.2 Design requirements

In an attempt to design and fabricate the microreactor, we considered the proceeding prerequisites so ensure their feasibility for photochemical reactions;

- ✓ The reactor must show minimal clogging and crystallization.
- ✓ Transparent to light for optimum penetration
- ✓ Larger surface area for maximum light required for reaction initiation.
- ✓ The type of glass material

Table 3-1. Types of glass material and their cut-off wavelengths

Types of glass	Wavelength cut-off (nm)
Pyrex	<275
Corex	<260
Vycor	<220
Quartz	<170

From Table 3-1 above, we can see that the best material for this application is the quartz glass because it can absorb light at a wavelength lower than 170nm which is sufficiently strong enough to break covalent bonds, in essence, shorter wavelength higher energy.

3.3 Experimental setup

The setup basically consists of a capillary glass made of quartz (length of 3.0, 7.0 and 11.0m with a constant internal diameter of 0.2mm), a magnetic stirrer to ensure homogeneity of the reaction mixture. A round bottom flask of 125/250ml where the reaction was mixed, a mirror for reflection to maximize solar intensity. Finally, the pump was to ensure a continuous flow of the system. The figure is a pictorial summary of the entire set up for the experiment conducted during the course of the research work. The set up was placed on top of building 5 mathematics department adjacent to the chemistry department of the King Fahd University of petroleum and minerals situated in Dhahran eastern province of the kingdom. The experiment was conducted from September 2015-March 2016.

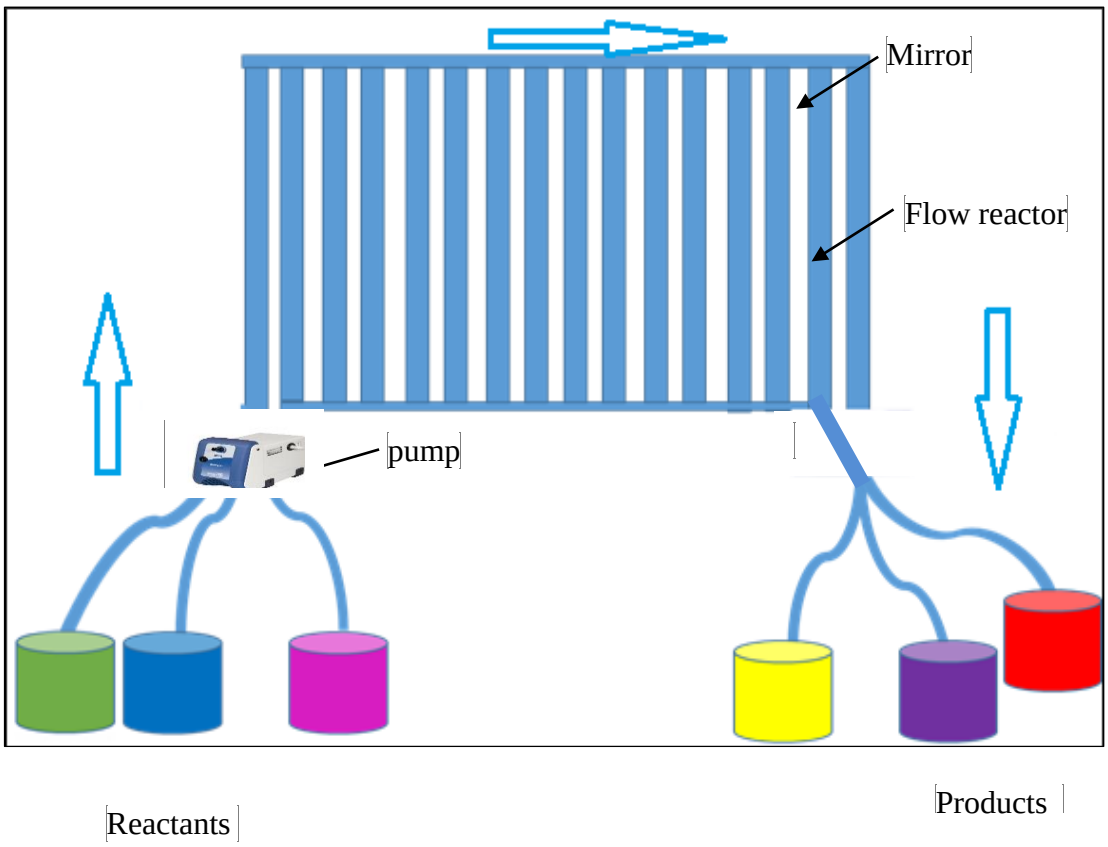

Figure 3-1. Reaction design and setup

3.3.1 Reactor fabrication

After setting a design for the reaction, we fabricated our capillary reactor following all the highlighted requirements as we have mentioned earlier.

After successfully employing the reactor for our reactions, we went ahead to fabricate a larger reactor of the same requirement in other to verify the efficiency. We increased the length of our capillary glass as a form of scaling up the reaction with increased residence time of the solution.

Figure 3-2. Fabricated capillary microreactor 1 (3.0m)

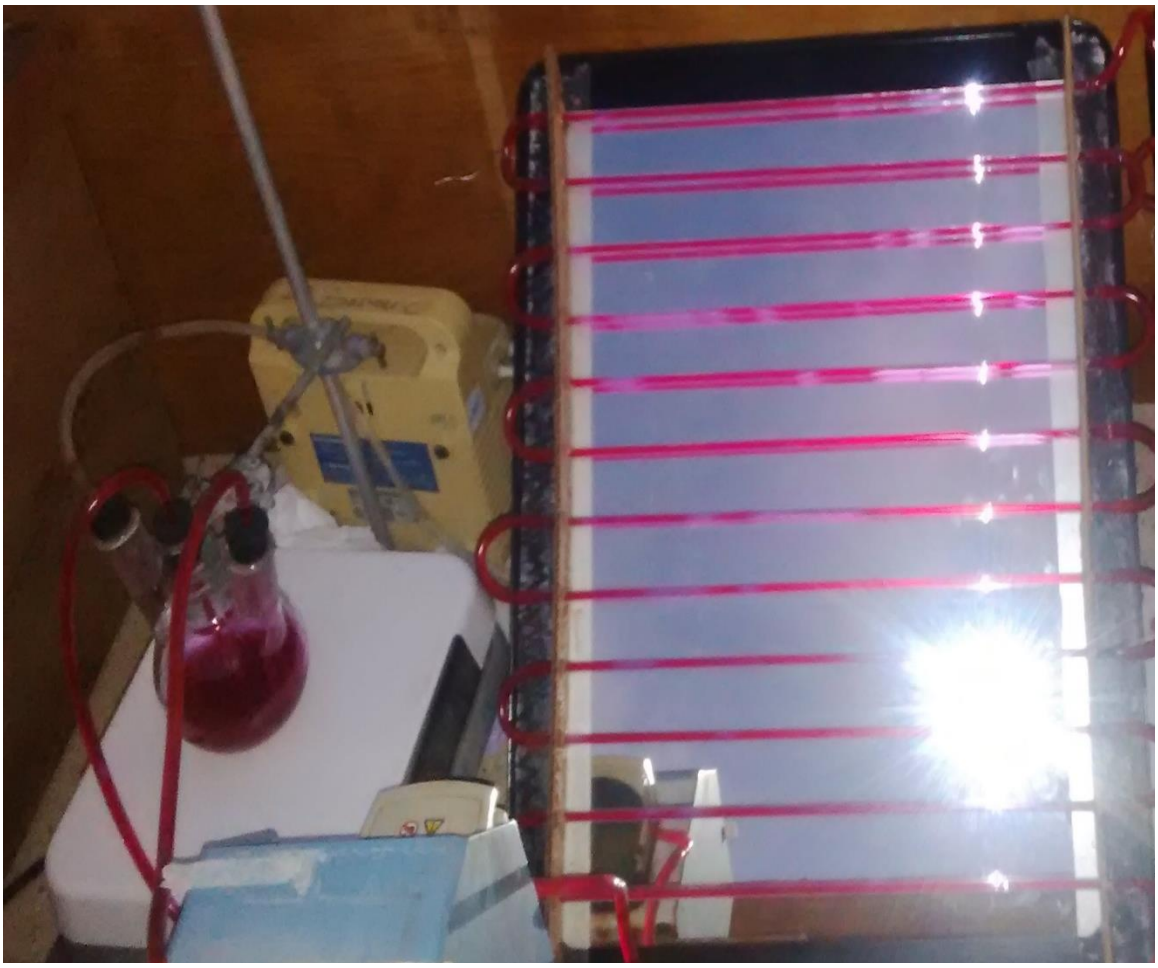

Figure 3-3. Fabricated capillary microreactor 2 (7.5m)

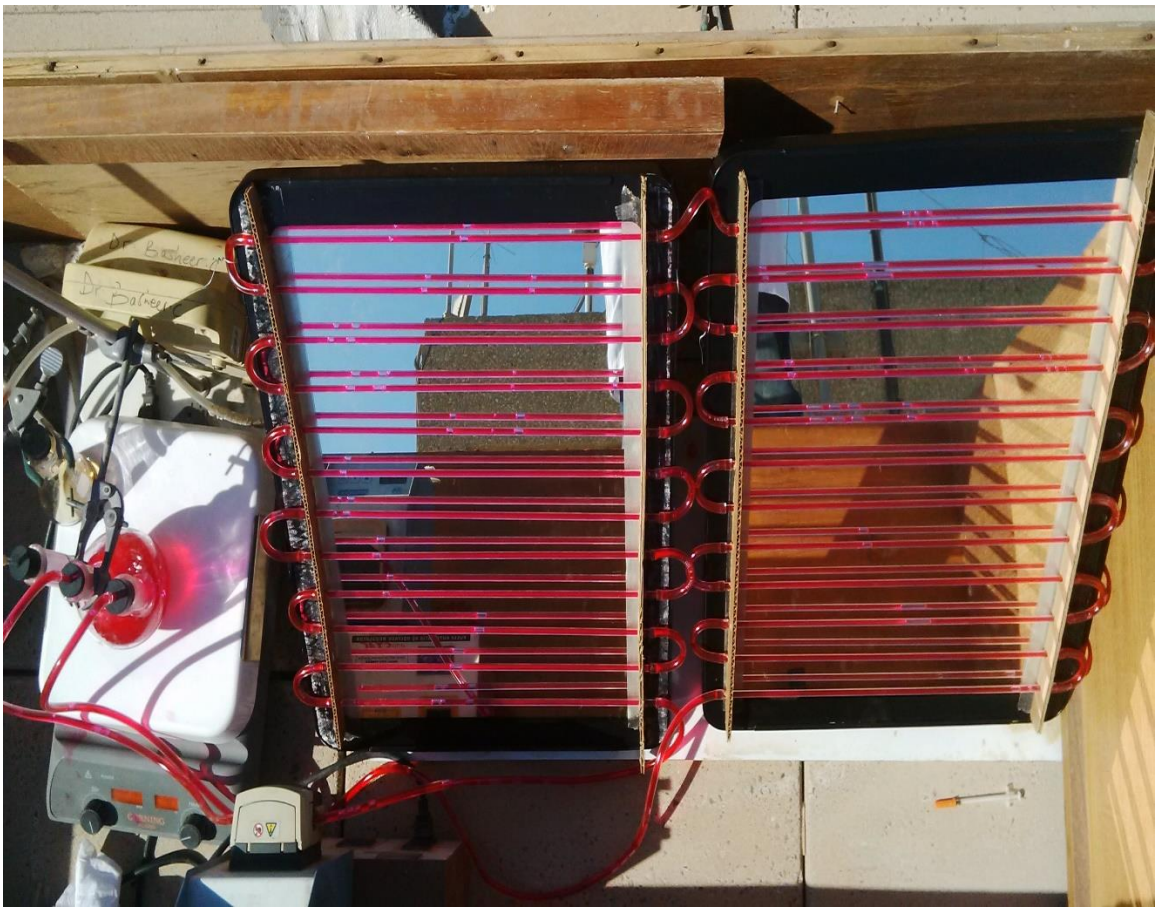

Figure 3-4. Fabricated capillary microreactor 2 (11.0m)

3.4 Instrumental Analysis

3.4.1 High-Performance Liquid Chromatography

High-Performance Liquid Chromatography (HPLC) Waters 2690 system (figure 3.3) with UV-Vis Diode array detector was used for the analysis and the stock solution ranging from 10 to 4000 mg/l was used for the calibration of the synthesis part of the study to cover the range of the concentration to be used in the experiments. For all of the concentration analysis, 2.0 mL of the solution was collected in a new glass vial, and 10µL is injected into the column for analysis. A chromatography column was used in the unit (3.9 ×300mm) µ Bonda Pak™ C18 stationary phase, while the mobile phase was acetonitrile (super grade 99.9% UPLC) and water with the ratio for the α-functionalization of the tertiary amine reactions 225nm wavelength 70:30 respectively. The same mobile phase combination was used for the photoacylation of 1,4-naphthoquinone. All runs with argon degassing of 20% of the mobile phase and the column conditioned using methanol HPLC grade of 99.9% at a temperature programming of 35℃ ±5. Samples run time was 15 minutes for all the samples.

3.5 Reactions performed

All reagents and solvents used to carry out the reactions in this work are commercially available in best grades.

In an attempt to test the microfabricated capillary flow reactors, we selected few reactions as models in order to come up with a conclusion on the efficiency of the device.

3.5.1 Reaction 1: Dehydrogenative Coupling reaction catalyzed by Rose Bengal.

An organic dye, Rose Bengal which generates excited singlet state were used as a photoredox catalyst for this reaction using sunlight irradiation. The introduction of our microreactor to miniaturize the reactants was able to enhance the product yield and also reduced reaction time.

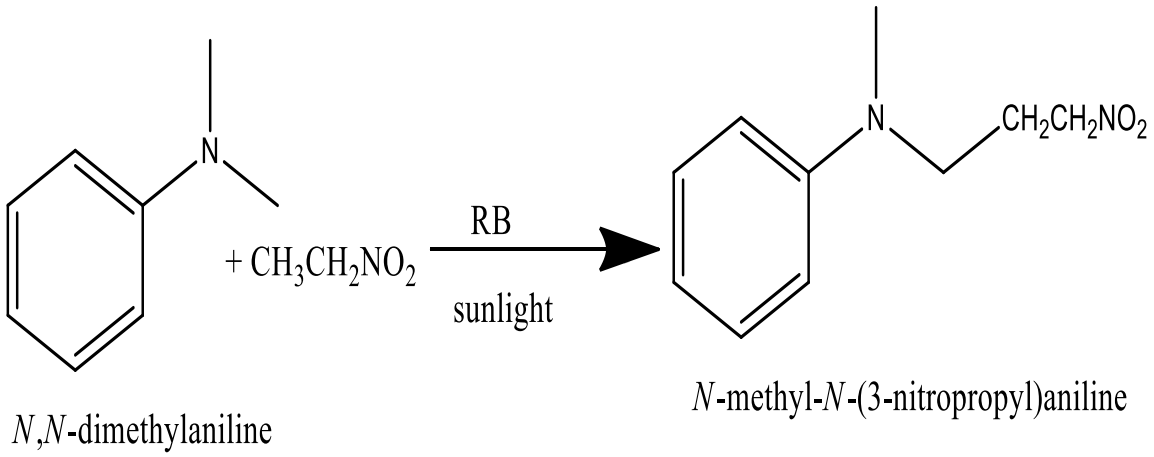

Figure 3-5. Oxidative Dehydrogenative coupling reaction

Procedure: N, N-dimethylaniline **(**20.9 mg, 0.17 mmol, 1.0 equiv.) of was added to a solution of RB (5.0 mg, 0.005 mmol, 5 mol %) in 1.0 ml nitroethane. The reaction mixture was stirred under sunlight irradiation. The reaction progress was monitored at interval using HPLC and TLC until a complete reaction was observed i.e. the optimal conversion of the desired product was isolated.

3.5.2 Reaction 2: Cyanation reaction catalyzed by Rose Bengal, acetic acid(cocatalyst).

α-Functionalization of tertiary amines is an important research part as it provides various functionalized amines which are particularly useful in pharmaceutical industry. However, the α-functionalization of tertiary amines using visible light irradiation is still not very successful as it can only involve some activated tertiary amines. For the inactivated substrates, the reactions are sluggish and some even do not provide products. Although the general formula of this type of reaction is *via* single electron transfer rather than involving singlet oxygen (Scheme 3), the detection of the reaction intermediates is still unsuccessful. The product of this reaction constitute one of the major component of some anti-tumour drugs such as saframycin and phthalascidin.

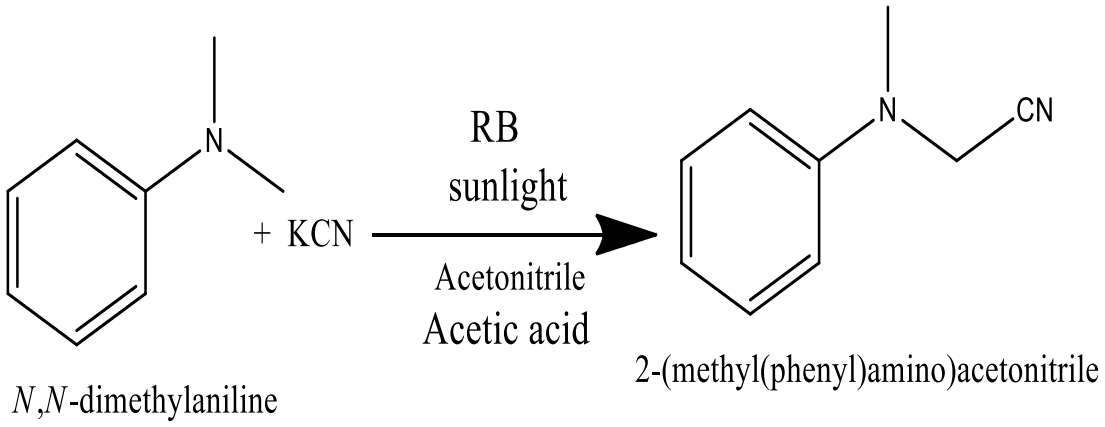

Figure 3-6. Oxidative Cyanation reaction

Procedure: N,N-dimethylaniline (20.9mg, 0.17mmol) and ACOH (28.6µL) were added to a solution of RB (5.0mg ,0.005mmol) in 1.0ml of CH_3CN followed by adding 7.8mg (0.11mmol) of KCN slowly. The mixture was passed through the reactor under sunlight irradiation, the final functionalized amines were collected and quantified using HPLC.

3.5.3 Reaction 3: Photoacylation of 1,4-naphthoquinone with an aldehyde

The above aforementioned reaction is a very important precursor in the synthesis of biologically active compounds. It was revealed in the literature that this particular reaction preceded under sunlight irradiation with about 89% yield using benzene as a solvent although the reaction time lasted for about 5 days to achieve the reported yield. However, the introduction of our fabricated microflow reactor, we were able to achieve a good yield with reduced reaction time.

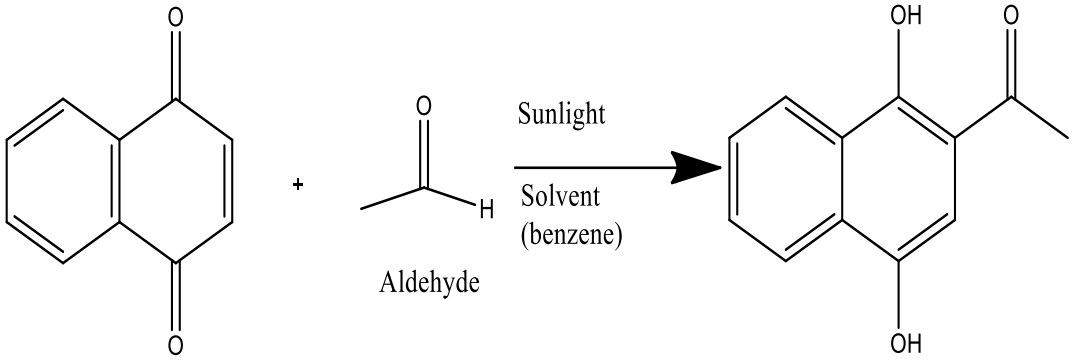

Figure 3-7. Photoacylation of 1,4-naphthoquinone with an aldehyde

Procedure: A solution of 1,4-naphthoquinone (1 mmol, 202.21mg), aldehyde (10 mmol, 577.88µL) and benzene (20 mL) was mixed and transferred into a round bottom flask, a stream of nitrogen was bubbled for 2 min. The mixture was pumped through the microreactor and irradiated under sunlight for about 21hours. The progress of the reaction was monitored using HPLC by collecting aliquot sample until the reaction was completed.

CHAPTER 4

RESULTS AND DISCUSSIONS

4.1 Reactor design

We designed a series of capillary reactors starting with 3.0, 7.5 and finally an 11.0m long. After gathering much information regarding the type of material suitable for this kind of reactions, we finally settled for Quartz to be the best of the different types of glass materials available as shown in Table 3-1 . The reason behind the choice of quartz was because it has a cut off wavelength below 175nm which is sufficient enough to break the C-H bonds.

4.2 Applications

Using visible light in organic synthesis has attracted an enormous interest in the recent time due to its renewability, free available in abundant and cleaner source of light. Amongst the distinct types of photosensitizers (organic and inorganic) that have been employed in the photochemical reaction under irradiation with visible light, Rose Bengal (metal-free) has shown interesting performance under sunlight irradiation. We set off our investigations using the fabricated continuous flow microreactor on alpha-functionalization of tertiary amine (N,N-dimethylaniline in this context) through an oxidative dehydrogenative coupling reaction with different organic dyes.

4.2.1 Dehydrogenative coupling reaction

We initiated out studies with dehydrogenative coupling reaction following the methodology discussed by Pan et al. [84]. The product was obtained as represented in reaction scheme 12. The capillary reactor 3.0 was employed for this reaction to establish the optimum reaction conditions.

4.2.2 Optimization of capillary internal diameter

Here we screened three different internal diameters (0.1, 0.2 and 0.3mm) of the quartz glass material based on availability and 0.2mm gave the best yield of the three diameters examined. This could be attributed to perhaps the residence time as a function of flow rate together with exposure time of the reaction mixture.

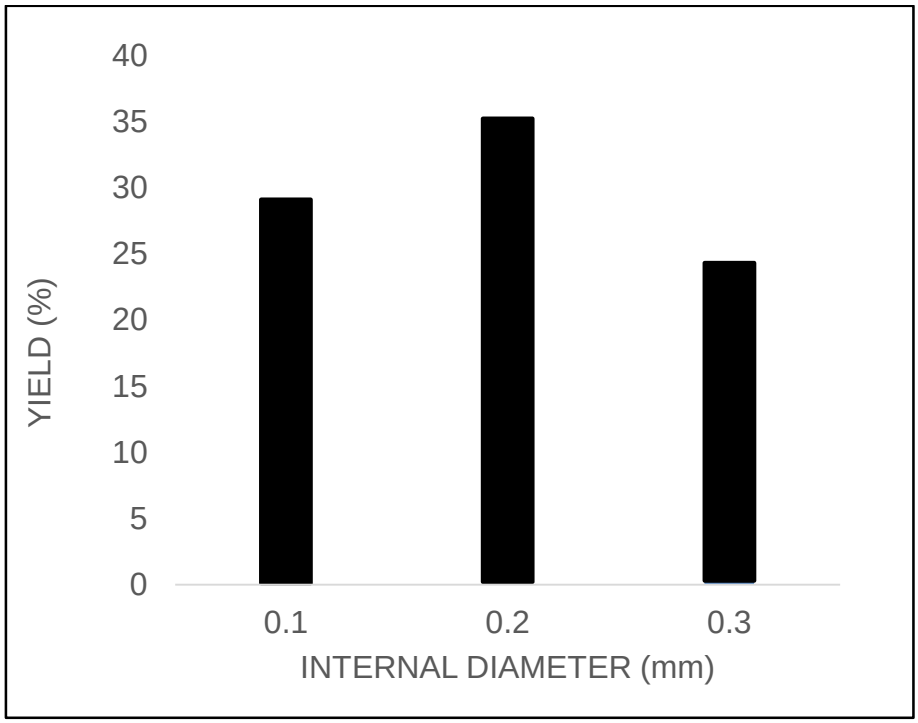

Figure 4-1 Optimization of capillary internal diameter

4.2.3 Optimization of organic dyes

We started our studies by first optimizing the reaction conditions by using different organic dyes. Interestingly, Rose Bengal proves to be the ideal dye for this reaction which has always known to be the best organic for this type of reactions as reported in the literature.

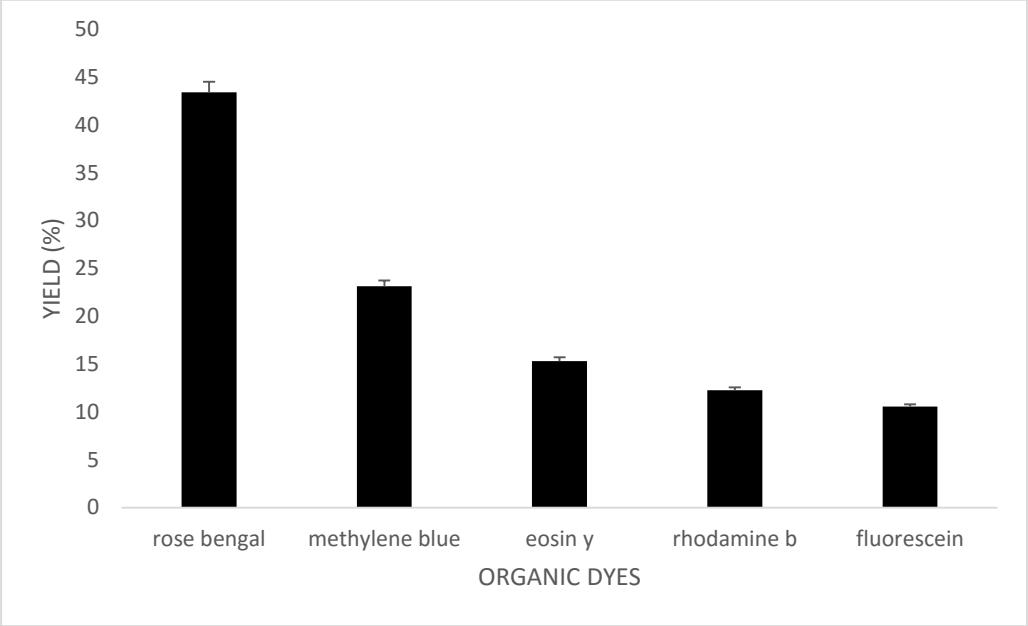

Figure 4-2. Optimization of reaction conditions using different organic dyes with acetonitrile

Table 4-1 Mass effect of RB on reaction yield

Expt no	Mass of RB	Sunlight	Time (hrs)	Yield (%)
4	0	Yes	14	0
5	1	Yes	14	21.6
6	2	Yes	14	25.7
7	3	Yes	14	33.4
8	4	Yes	14	38.5
9	5	Yes	14	43.0
10	6	Yes	14	42.1
11	7	Yes	14	40.0
12	8	Yes	14	39.9

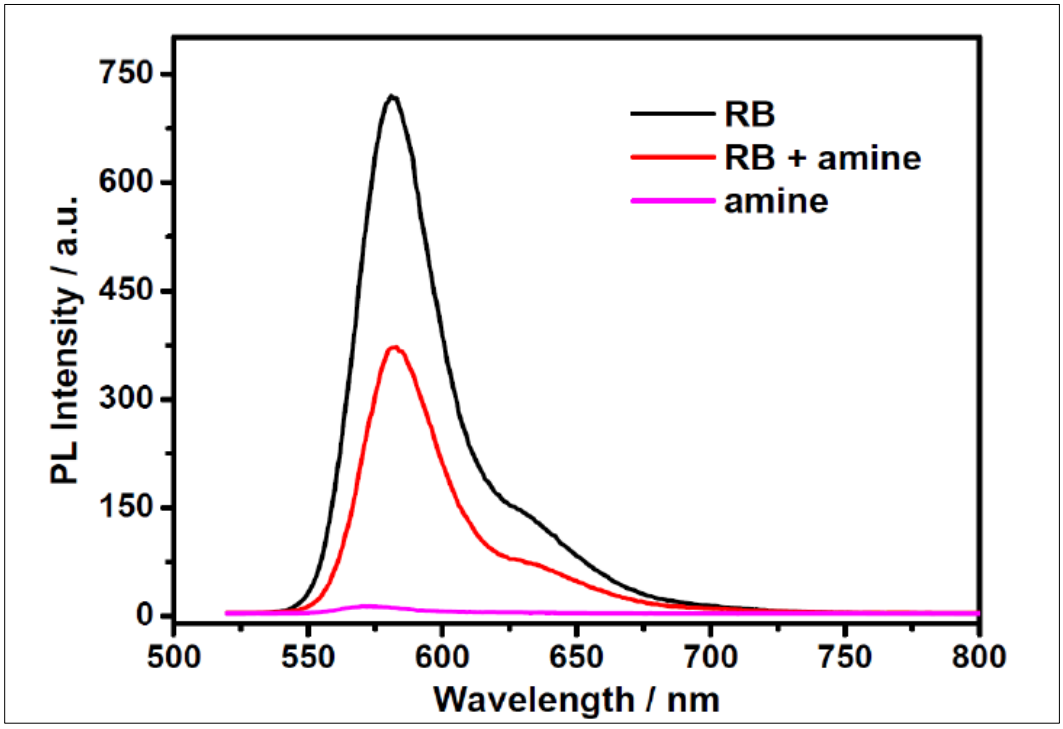

Figure 4-3. Quenching studies for Rose Bengal [94].

As seen in Figure 4-3 above, the addition an amine to Rose Bengal quenches it after its excitation following the absorption of a photon of light. The quenching process returns RB back to the ground state after an amine is added via the single electron transfer process as reported by Pan et al [82]. The triplet state of RB is quenched totally by O_2 in polar aprotic solvents, in so doing producing singlet O_2 and a superoxide radical ion. It is this property that gives RB the edge in the wider range of applications over other types of organic dyes.

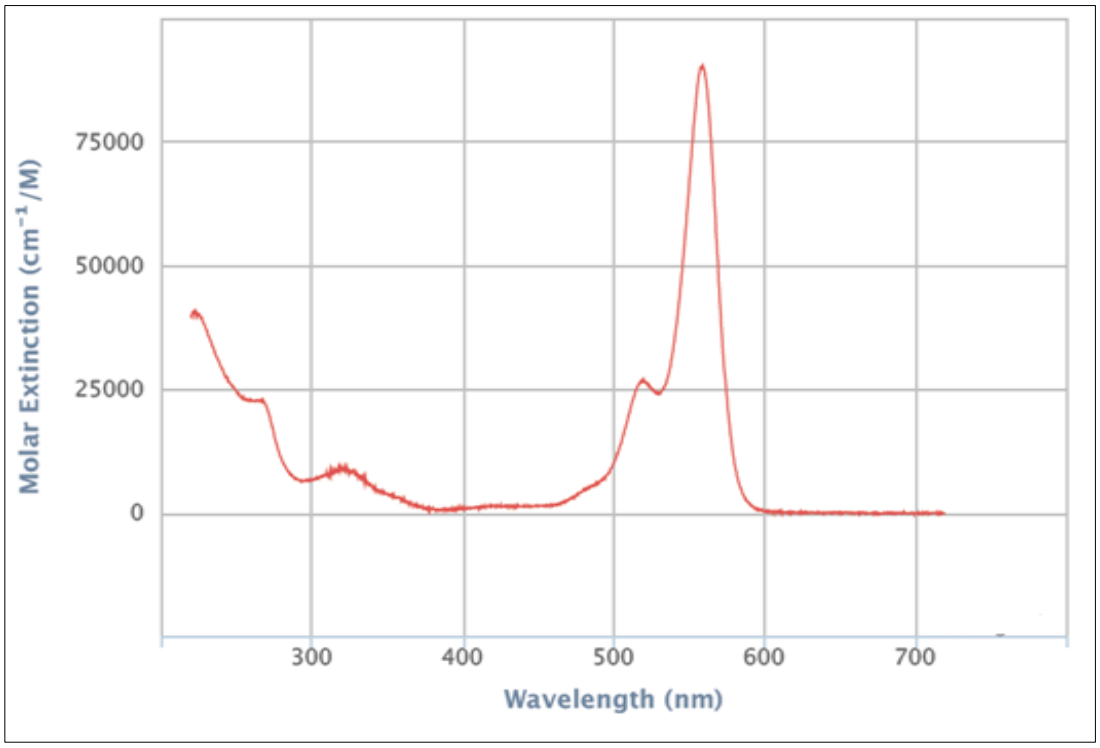

Figure 4-4. Extinction coefficient of Rose Bengal [95].

The large extinction coefficient of Rose Bengal makes it distinct from other types of dyes which could possibly add to the reason of its success in this type of reactions.

4.2.4 Optimization of flow rate

Having had the best dyes at hand, we further optimized the flow rate of the continuous system. We used three different flow rates 0.2, 0.3 and 0.4mL/min. We observed a decreasing trend in the yield as the flow rate increases. For this reason, we chose 0.2mL/min flow rate as our optimum flow rate.

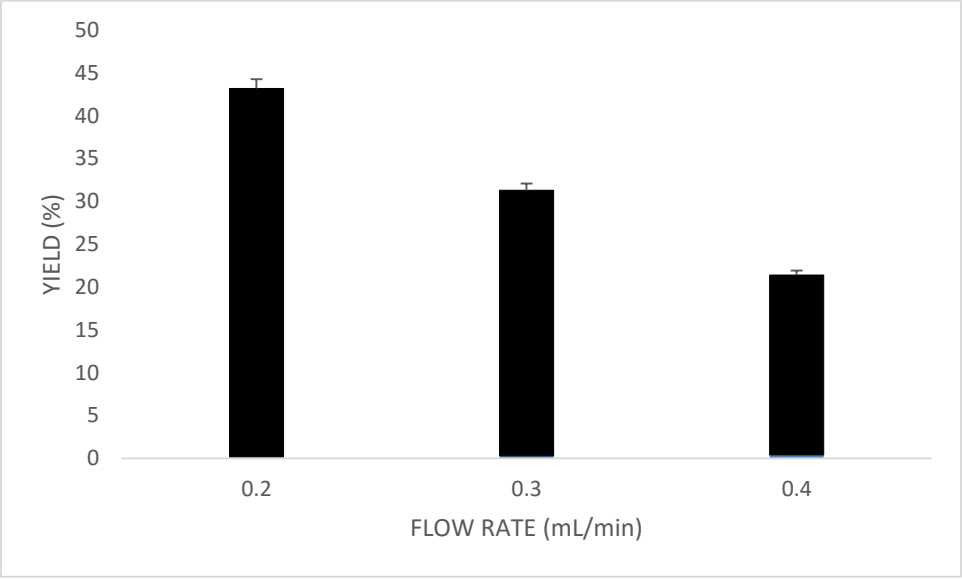

Figure 4-5. Optimization of flow rate with rose Bengal in acetonitrile.

In trying to choose the best flow rate for efficient yield, we varied the flow rate of the reactor pump and the results are presented in the Figure 4-5 above.

Following the results generated from the optimization of reaction conditions, we were able to establish that Rose Bengal was the best sensitizer as far as this reaction is concerned and performance was optimum at a flow rate of 0.2mL/min of the reactor pump. Unfortunately, the conversion was only 43% after working on the optimum reaction conditions after 14hours which are in close agreement with a work reported by Yuanhang Pan et al [84] using an analogous substrate as ours. The product was confirmed using ^{1}H NMR and ^{13}C NMR. When the same reaction was placed in a quartz tube (batch system) only trace amount of the product was observed under the same reaction time.

To confirm the effect of sunlight intensity on the reaction rate, we carried out the reaction under two different conditions taking the dark condition as a control for the progress.

Table 4-2. Dehydrogenative coupling Reactions under different sunlight conditions, RB in CH_3CN, n=3

Expt no.	Time (hrs)	direct sunlight	cloudy daylight	Dark
		Yield (%)	Yield (%)	Yield (%)
1	10	19.0 ±0.48	10.0 ±0.25	0
2	12	25.0 ±0.63	11.0 ±0.28	0
3	14	43.0 ±1.08	15.0 ±0.38	0

Table 4-2 above presents the variation in the yield as the irradiation condition drops from direct sunlight to cloudy daylight, sadly, no conversion was observed when the reaction was monitored in the dark. Based on the Data presented in the table, it is obvious that the sunlight intensity has an adverse contribution to the success of the reaction efficiency.

Table 4-3 Showing comparison between this study and the literature

Reaction	**Light source**	**Time (hrs)**	**Yield (%)**	**System**	**Ref.**
Dehydrogenative coupling reaction	LED	96	48	Batch	Pan et al 2011.
Dehydrogenative coupling reaction	Sunlight	14	43	Continuous flow	This work

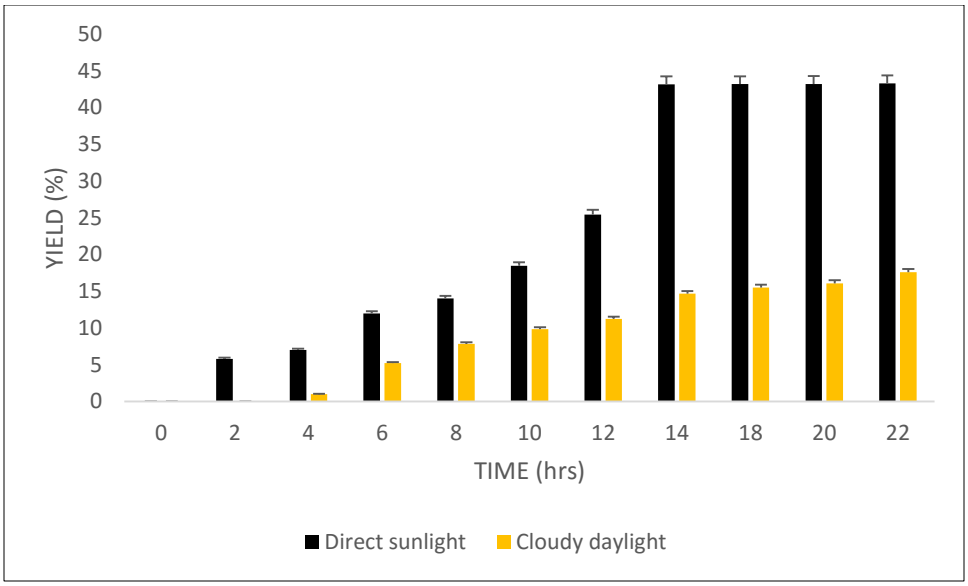

Figure 4-6. The progress of dehydrogenative coupling reaction.

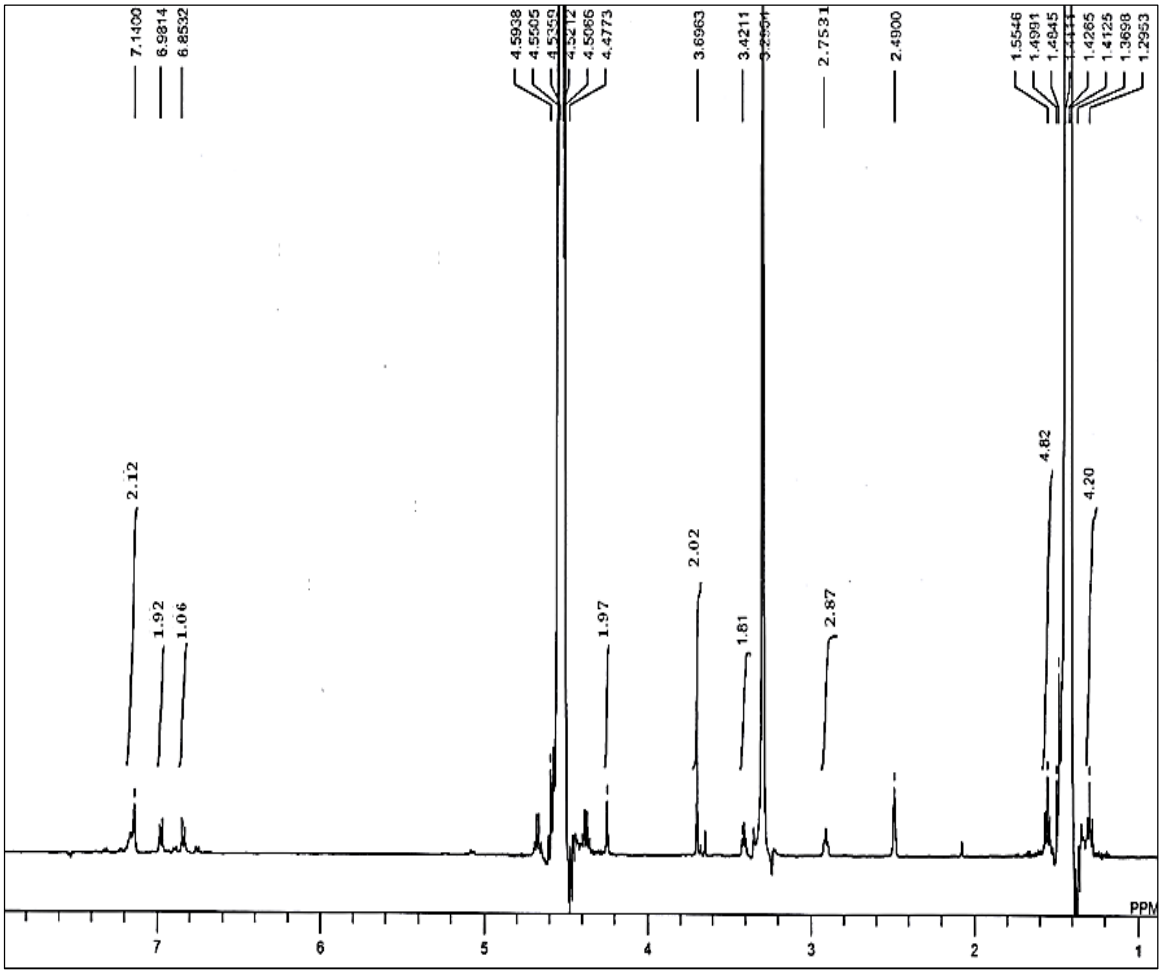

Figure 4-7. ^{1}H NMR for the crude dehydrogenative coupling reaction

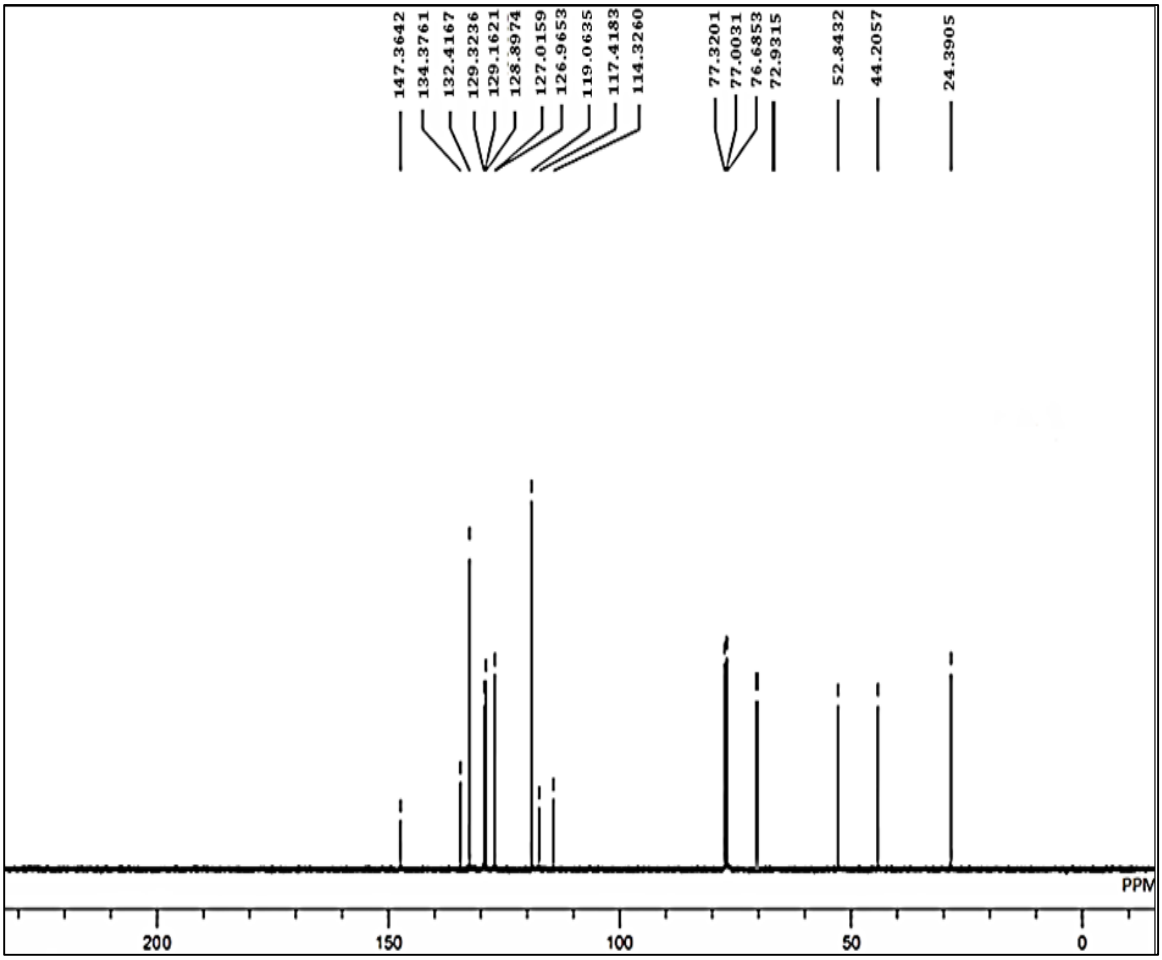

Figure 4-8. ^{13}C NMR for the crude dehydrogenative coupling reaction.

4.2.5 Cyanation reaction

After we have established an optimum reaction condition based on the dehydrogenative coupling reaction, our studies proceeded with investigating cyanation reaction. We assessed the oxidative photochemical reaction of the aforementioned tertiary amine in the presence of Rose Bengal (sensitizer) and acetic acid as a co-catalyst, KCN as the CN source.

Interestingly, we were able to isolate a good yield (80%) of the desired alpha-aminonitrile. Acetic acid has shown to be very significant in the conversion. This evidence can be ascribed to the liberation of hydrogen cyanide in the presence of acetic acid, [75] hence, only trace amount of CN^- is present in solution. However, acetic acid acts as a co-catalyst in this reaction [75]. In an attempt to validate the theory, the reaction was carried out in the absence of acetic acid, to our greatest surprise, only trace amount of the anticipated product was observed.

Table 4-4. Effects of additive in reaction yield with Rose Bengal, acetonitrile and 0.2mL/min flow rate, n=3.

Expt no.	CN^- source	Additive	Time (hrs)	direct sunlight Yield (%)	cloudy daylight Yield (%)
4	KCN	AcOH	18	47.0 ±1.18	30.0 ±0.75
5.	KCN	AcOH	30	64.0 ±1.60	37.0 ±0.95
6	KCN	AcOH	45	80.0 ±2.0	38.0 ±0.95
7.	KCN	_	45	42.0 ±1.05	Trace

From the result presented in Table 4-4 above, it demonstrated a variation in the conversion where a better yield was recorded for the direct sunlight and otherwise was observed when the reaction was monitored under cloudy daylight.

As solvents have effects on most photochemical reactions reported, polar aprotic solvents have been established to give excellent yields (DMF, THF, and MeCN). Although, MeCN has been reported to be the best [74].

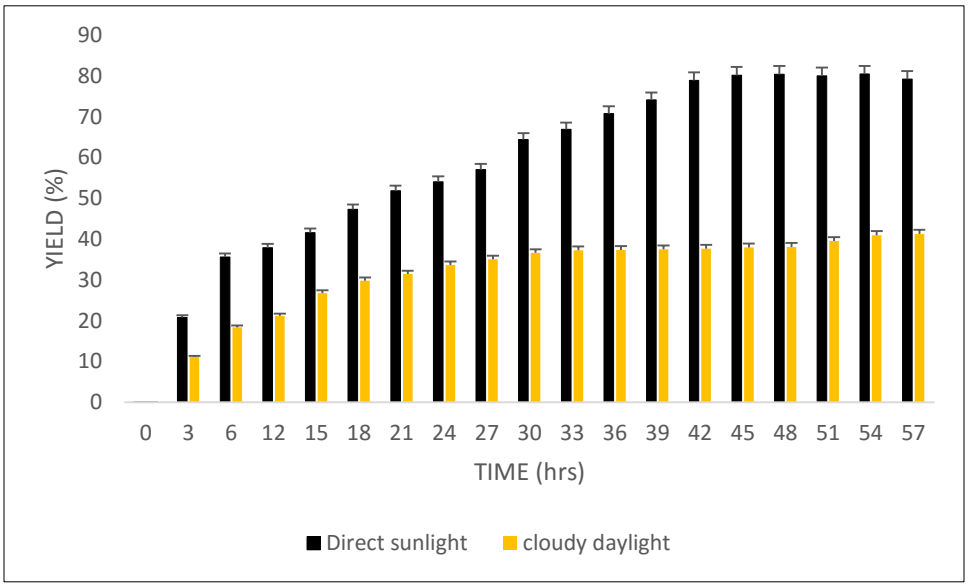

Figure 4-9. The progress of reaction for cyanation reaction using a 3.0m capillary reactor.

In order to confirm the trend observed with reduced reaction time following the increased residence time of the reaction mixture, we designed another microreactor of about 7.5m long. The aftermath of this reaction was an interesting one, a reduction in reaction time of about 15hrs was achieved and a slight increment in yield (about 3%).

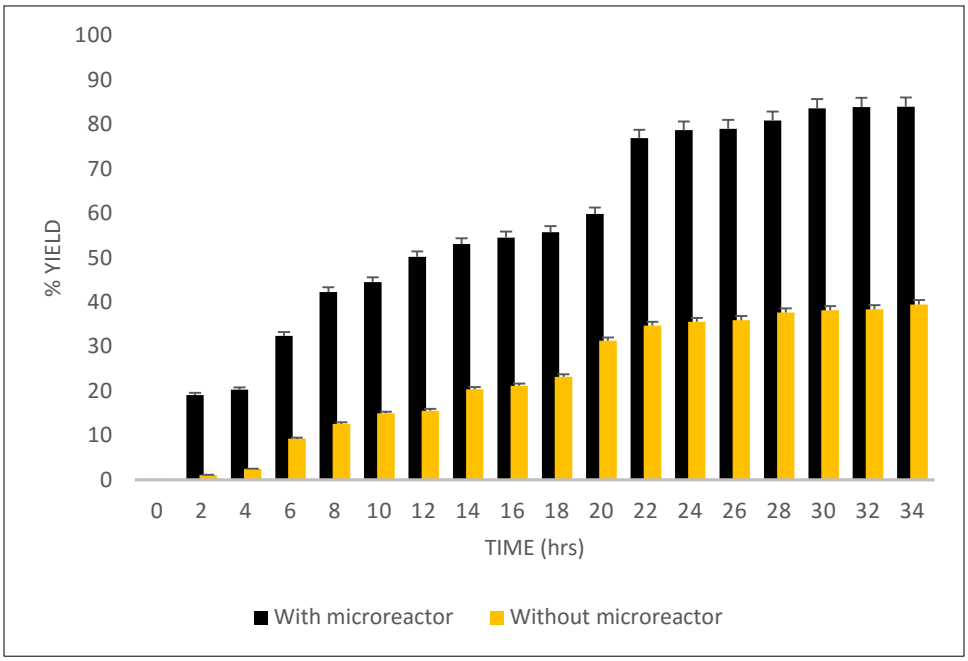

Figure 4-10. The reaction progress for cyanation reaction using a 7.5m capillary reactor.

To further affirm this trend, we used the 11.0m capillary reactor and interestingly, there was an improvement in the reaction time, however, the yield was about 79% after 24hrs of reaction which shows a good trend irrespective of the yield. A comparison between a continuous and a batch system, obviously, the yield was better-off with the use of a microreactor.

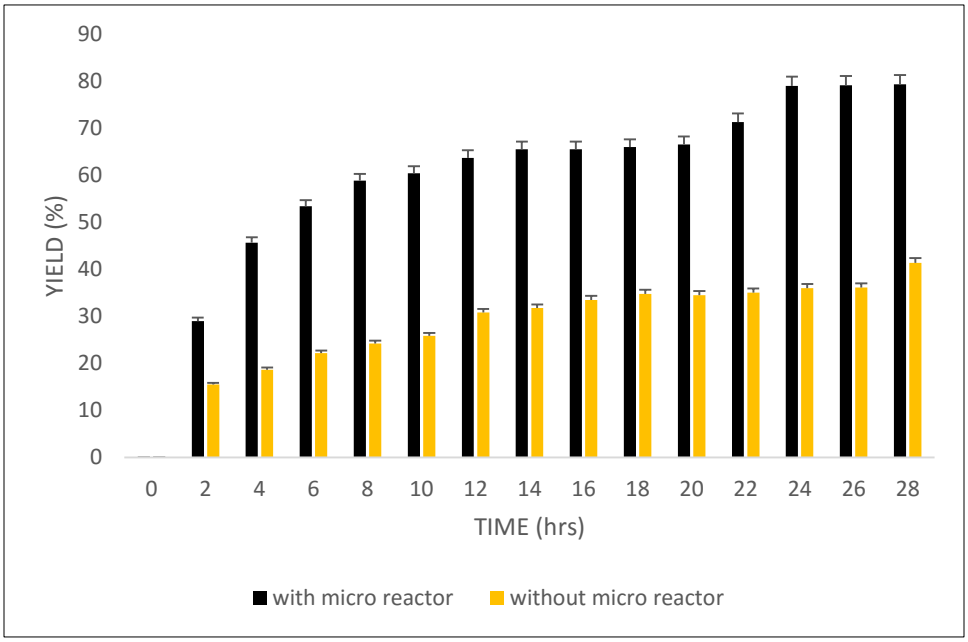

Figure 4-11. The reaction progress for cyanation reaction using 11.0m capillary reactor.

The two larger capillary reactors were used for the reaction and the yield of 81 and 79% was obtained respectively for 7.5 and 11.0m capillary reactors. The reactions were performed under direct sunlight condition and compared to the batch system which is represented as ‘without microreactor’ in the figure above.

Table 4-5 Reactor size comparison

Reactor size (m)	Time (hrs)	Yield (%), n=3
3.0	45	80.0 ±2.0
7.5	30	83.0 ±2.08
11.0	24	79.0 ±1.98

Table 4-6 Showing comparison between this work and literature

Reaction	Light source	Sensitizer	Time (hrs)	Yield (%)	System	Ref.
Oxidative cyanation	LED	$[Ir(tbp\text{-}py)_2(bpy)]PF_6]$	96	84	Batch	Rueping et al. 2011
Oxidative cyanation	Sunlight	Rose Bengal	24	≃ 80	Continuous flow	This work

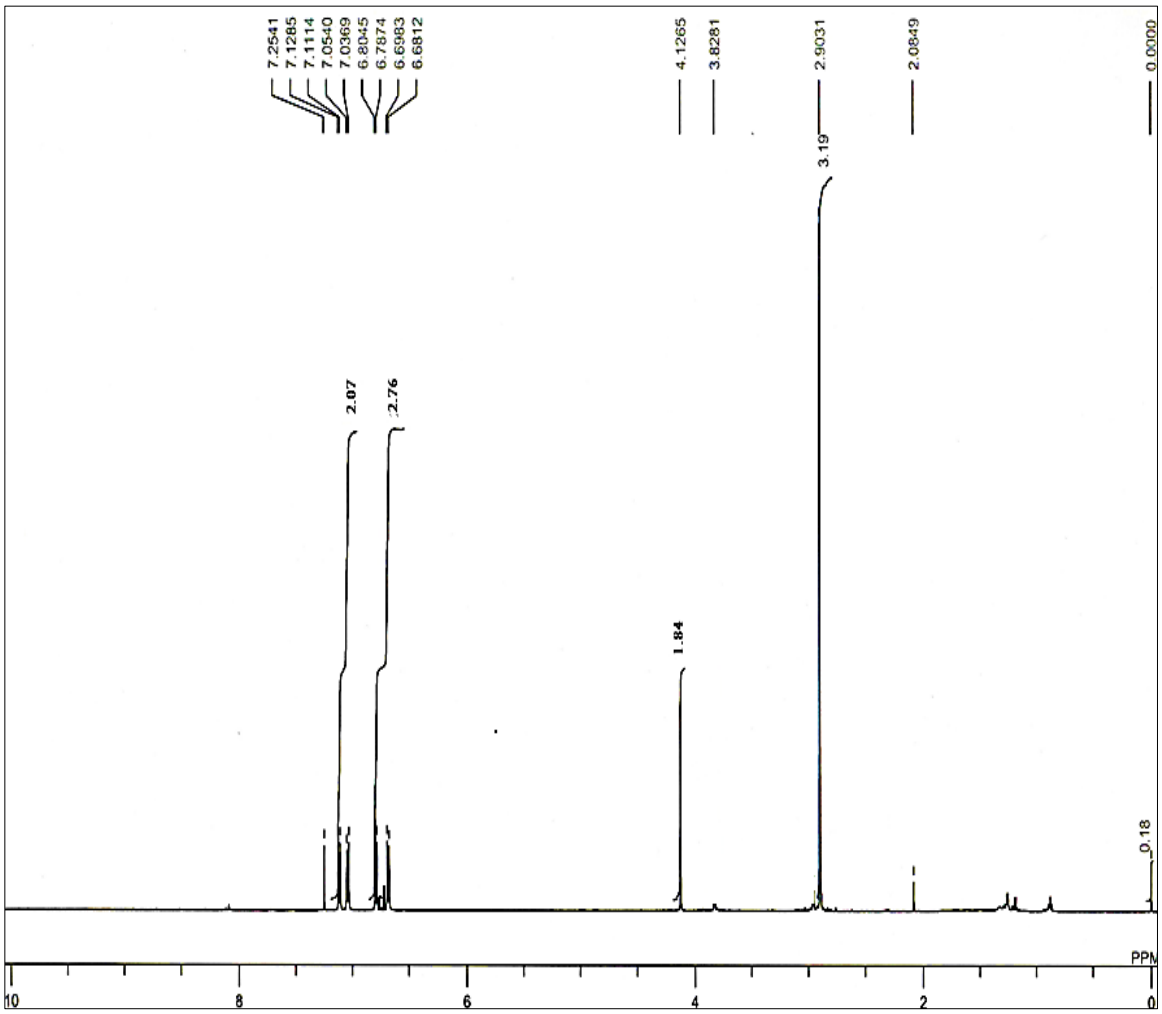

Figure 4-12. ^{1}H NMR for the pure product 2-(methyl(phenyl)amino) acetonitrile. in $CDCl_3$

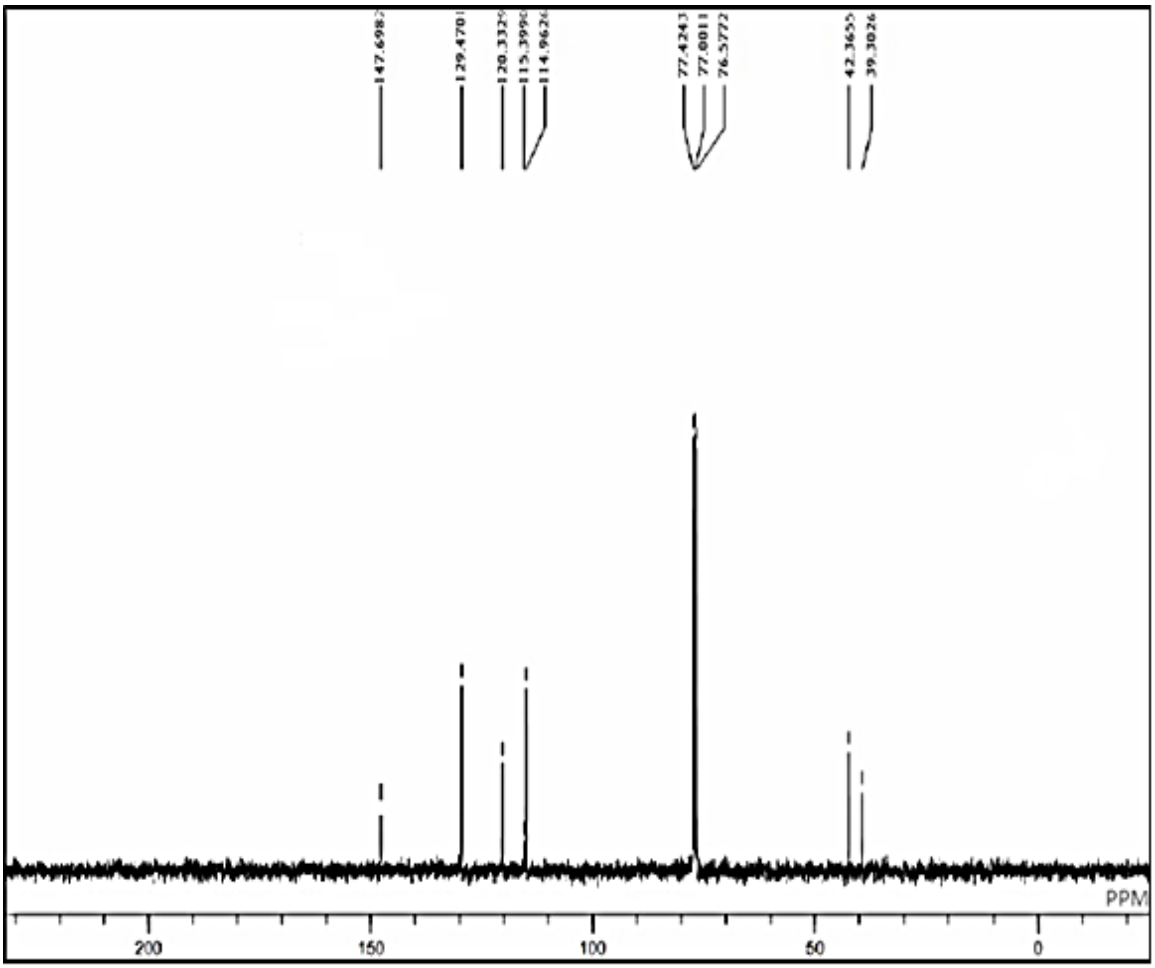

Figure 4-13. ^{13}C NMR for the pure product in $CDCL_3$

4.2.6 Photoacylation of 1,4-naphthoquionone with an aldehyde.

Finally, we carried out this reaction to corroborate the efficiency of the capillary microreactor. A similar reaction of this kind was reported by Benites [82] which was carried out under a batch system in sunlight irradiation. Although, they used furfural as their aldehyde, benzene as the solvent media and ended up with about 81% of the desired product after 5 days of irradiation. We used ethanal in benzene and a yield of about 64% after 21 hours of reaction (approximately two and a half days) was obtained. This could be attributed to the continuous system that was put in place with the microreactor which allows easy and homogeneous penetration of the sunlight. The essence of this reaction was to fully confirm if the reactor contributes to the pace of reaction.

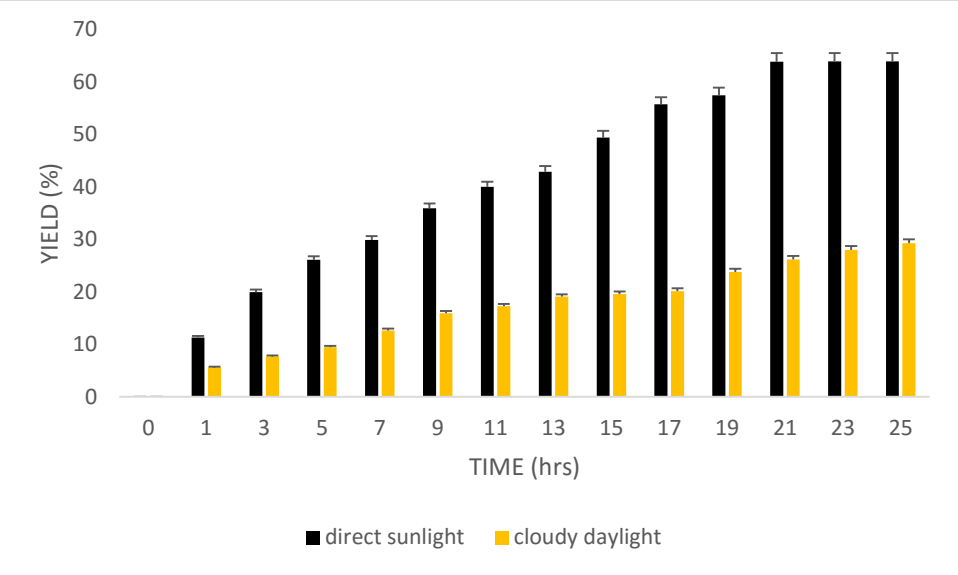

Figure 4-14. The reaction progress for the reaction.

The reaction was completed after 21hours yielding about 64% of the desired product. As shown on the plot, the reaction was carried out under two sunlight condition with direct sunlight given a better and faster product. This is a significance of sunlight intensity. The higher the intensity, the better the reaction.

Table 4-7 Showing comparison between this work and literature

Reaction	Light source	Time (hrs)	Yield (%)	System	Ref.
Photoacylation of 1,4-nalphthoquinone	Sunlight	45	81	Batch	Lorna et al. 2013
Photoacylation of 1,4-nalphthoquinone	Sunlight	21	64	Continuous flow	This work

CHAPTER 5

CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

We successfully designed a series of three different capillary microreactors which were then employed for the synthesis carried out in this study. The 3.0m capillary reactor was used for the dehydrogenative coupling and photoacylation reactions. After successfully achieving an optimized reaction condition, the same reactor was used for the cyanation reaction which is where most of our interest lies. Afterward, we used the 7.5 and 11.0m reactors for scaling up the cyanation since it was the first time such a reaction is conducted.

The use of capillary reactor has shown a great advantage to synthesis thereby reducing reaction time. Also, the reactions under sunlight irradiation have proven success since sunlight is in abundance here in the kingdom. In essence, the combination of sunlight and microreactor has shown an improvement in synthesis. Furthermore, we were able to prove the use of acyclic amines for the aforementioned reactions which was a good support of the idea of Magnus et al. who as well used a derivative of the acyclic amines in his study. For the first time, we employ an organic dye alongside acetic acid (cocatalyst) and a welcoming result was obtained. Acetic acid proved to be very vital in the reaction, and when the reaction was carried out in its absence, the yield was remarkably affected. In addition, we were able to establish how the capillary reactor helps in shortening the reaction time in Friedel craft acylation for the development of acylated hydroquinones.

5.2 Recommendations

In the Future the, more efforts should be put in place in seeing the possibility of regenerating the organic dyes and evaluate them after regeneration.

Also, an alternative should be provided in a way of bringing sunlight into the lab (a form of sunlight-mimicking) technology to bypass the uncertainty in weather stability.

Further studies should work on the structural rationale behind the efficiency of Rose Bengal over other organic dyes, however, it has been stated already that it has a large extinction coefficient.

Finally, more emphasis should be given to ways on how to explore the continuous system for other application aside photochemical reactions.

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